TWENTY-SECOND INTERNATIONAL SYMPOSIUM ON FREE RADICALS

BOOK OF ABSTRACTS

Doorwerth, The Netherlands

6-10 September 1993

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ACKNOWLEDGEMENT

This conference is financially supported by:

Royal Dutch Academy of Sciences (KNAW)
Foundation for Fundamental Materials Research (FOM)
Physics Foundation
University of Nijmegen
European Office of Aerospace Research and Development (AFSC)
Coherent Benelux
EG&G Instruments Nederland
La Vision 2D-Messtechnik GmbH
Melles Griot
Optilas BV
Quantel
Radiometer Nederland BV
SOPRA

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE September 1993	3. REPORT TYPE AND DATES COVERED C Conference Proceedings

4. TITLE AND SUBTITLE Twenty-Second International Symposium on Free Radicals	5. FUNDING NUMBERS F6170893W0819
6. AUTHOR(S) Conference Committee	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Nijmegan Department of Molecular and Laser Physics Toernooiveld 6525 ED Nijmegan The Netherlands	8. PERFORMING ORGANIZATION REPORT NUMBER N/A
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) EOARD PSC 802 BOX 14 FPO 09499-0200	10. SPONSORING/MONITORING AGENCY REPORT NUMBER CSP-93-1037

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.	12b. DISTRIBUTION CODE A

13. ABSTRACT (Maximum 200 words)

Conference proceedings from the 22nd International Symposium on Free Radicals held 6-10 September 1993 in Doorwerth, The Netherlands.

14. SUBJECT TERMS	15. NUMBER OF PAGES 105
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19, SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18
298-102

Programme

Sunday 5 September

14.00	REGISTRATION DESK OPEN	
19.00	WELCOME RECEPTION	

Monday 6 September

8.55	OPENING	
9.00		**M.N.R. Ashfold** (University of Bristol, UK) *Photofragment spectroscopy of free radicals*
9.45		**D.M. Neumark** (University of California, Berkeley, USA) *Photodissociation dynamics of free radicals*
10.30	COFFEE BREAK	
11.00		**F. Temps** (MPI Strömungsforschung, Göttingen, FRG) *Rotation vibration state specific studies of the unimolecular dynamics of highly vibrationally excited molecules*
11.45		**E. Tiemann** (University of Hannover, FRG) *High resolution spectroscopy of fragments from photodissociation*
12.30	LUNCH	
14.00		**Poster session A -- Introduction**
15.00		**Poster presentation** *with tea* **Product exhibitions**
18.00	DINNER	
19.30		**E. Boersma** *"A bridge too far"*

Tuesday 7 September

9.00		**E.F. van Dishoeck** (University of Leiden, NL) *Free radicals in interstellar space*
9.45		**W. Cooksy** (Harvard University) *Microwave spectra and structure of* HC_3O
10.30	COFFEE BREAK	
11.00		**J.J. ter Meulen** (University of Nijmegen, NL) *Rotational energy transfer of OH in collisions with He, Ar and* H_2
11.45		**P.J. Dagdigian** (Johns Hopkins Univ., Baltimore, USA) *Rotationally and electronically inelastic scattering of diatomic free radicals*
12.30	LUNCH	
14.00		*Excursion to Palace 't Loo*
18.00	DINNER	
19.30		**Poster session B -- Introduction**
20.30		**Poster presentation** *with coffee*

Wednesday 8 September

9.00		**C. Demuynck** (University of Lille, France) *Bridged structures in small molecules and ions from their millimeter waves spectrum*
9.45		**Y. Endo** (University of Tokyo, Japan) *Fourier-transform microwave spectroscopy of free radicals and radical complexes*
10.30	COFFEE BREAK	
11.00		**J. Hutson** (University of Durham, UK) *Potential energy surfaces from the spectroscopy of open-shell and closed-shell van der Waals complexes*
11.45		**T.A. Miller** (Ohio State University, USA) *Laser induced fluorescence spectroscopy of complexes containing free radicals*
12.30	LUNCH	
14.00		*Free afternoon/visit to Molecular and Laser Physics laboratory at the University of Nijmegen*
18.30	DINNER	
19.30		**Poster session C -- Introduction**
20.30		**Poster presentation** *with coffee*

Thursday 9 September

9.00		**G. Guelachvili** (University of Paris-Sud, France) *Infrared spectroscopy of transient molecules*
9.45		**E.H. Fink** (University Wuppertal, FRG) *Near-infrared Fourier-transform emission spectroscopy on free radicals*
10.30	COFFEE BREAK	
11.00		**G. Hancock** (University of Oxford, UK) *Radicals and Ions in plasmas used for semiconductor processing*
11.45		**J. Wolfrum** (University of Heidelberg, FRG) *Microscopic and macroscopic dynamics of free radicals in combustion*
12.30	LUNCH	
14.00		*Excursion to Kröller-Müller Museum*
19.30	CONFERENCE DINNER	

Friday 10 September

9.00		**A. Bieske** (Basel, Switzerland) *Spectroscopy and dynamics of small ionic clusters*
9.45		**C.A. de Lange** (University of Amsterdam, NL) *Rotationally resolved REMPI-PES of OH and NH*
10.30	COFFEE BREAK	
11.00		**P.A. Hackett** (Steacie Institute, NRC Canada) *Photo excitation and relaxation dynamics of small transition metal clusters*
11.45		**A.J. Merer** (University of British Columbia, Canada) *Transition metal-containing radicals: order and complexity*
12.30		CLOSING
12.40	LUNCH	
	DEPARTURE	

INVITED LECTURES

PHOTOFRAGMENT TRANSLATIONAL SPECTROSCOPY

M.N.R. Ashfold, I.R. Lambert, D.H. Mordaunt, G.P. Morley and S.H.S. Wilson
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The technique of H atom photofragment translation spectroscopy, pioneered by Welge and coworkers at Universität Bielefeld,[1-3] has recently been used in Bristol to further investigate details of the near ultraviolet photodissociation of the molecules NH_3, PH_3, H_2S and CH_3SH, and of the Lyman-α photolysis of H_2O, H_2S, HCN, and CH_4. In each case, the structure evident in the H atom time-of-flight (TOF) spectrum provides new, detailed information about the energy disposal in the partner molecular fragment and thus about the dynamics of the primary photodissociation process. The following examples will be considered in some depth:

(i) HCN photolysis at 121.6 nm. The H atom TOF spectrum is dominated by a single peak, consistent with formation of vibrationless CN fragments in their $A^2\Pi$ excited electronic state.[4] This example serves to illustrate the power of photofragment translational spectroscopy as a method of establishing product branching ratios.

(ii) H_2S photolysis at 218.2 nm.[5] The H atom TOF spectrum shows features due to primary photolysis of H_2S and due to the secondary photolysis of the nascent SH(X) fragments. Modelling these spectra provides improved values for the D_0(S-H), the bond dissociation energy of the SH radical in its ground electronic state.

(iii) H_2S photolysis at 121.6 nm.[2,5] Analysis of the H atom TOF spectrum shows the partner SH fragment to be formed in its $A^2\Sigma^+$ excited electronic state, with a rotational state population distribution that extends up to the highest possible quasi-bound rovibrational level. The deduced rovibrational term values, together with the S-H bond strength determined above, enable us to provide a reliable potential energy function for the $A^2\Sigma^+$ state of SH.

(iv) H_2O photolysis following excitation to its $\tilde{B}^1A_1$ state at 121.6 nm. Structure due to population of high rotational states of both the ground ($X^2\Pi$) and excited ($A^2\Sigma^+$) states of the partner OH fragment are evident in the H atom TOF spectrum. Analysis of OH fragment rotational state population distributions provides further clues as to the relative importance of the possible non-adiabatic routes ($\tilde{B} \rightsquigarrow \tilde{A}$ electronic Coriolis coupling and $\tilde{B} \rightsquigarrow \tilde{X}$ transfer via a conical intersection in the H-OH dissociation channel) whereby $\tilde{B}$ state H_2O molecules can dissociate to ground state fragments.

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FAST BEAM STUDIES OF FREE RADICAL PHOTODISSOCIATION

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We have developed a novel technique for studying the photodissociation spectroscopy and dynamics of free radicals. In our experiment, radicals are generated by laser photodetachment of a fast (6-8 keV) mass-selected negative ion beam. The resulting radicals are photodissociated with a second laser, and the photofragments are collected and detected with high efficiency using a microchannel plate detector. The overall process is :

$$ABC^- \xrightarrow[h\nu_1]{} ABC + e^- \xrightarrow[h\nu_2]{} A + BC, AB + C$$

Two types of fragment detection schemes are used. We can scan the photodissociation laser $h\nu_2$ and measure the total photofragment yield as a function of ν_2. We also perform photodissociation dynamics using a photofragment coincidence detection scheme based on the two-particle position and time sensing detector developed by Los.[1] In these experiments, $h\nu_2$ is fixed, and we determine photofragment kinetic energy, angular distributions, and overall yield for each product channel. Thus far, photodissociation dynamics experiments using this detector have been carried out for O_2, N_3, and CH_2NO_2, and results for these systems will be presented.

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ROTATION VIBRATION STATE SPECIFIC STUDIES OF THE UNIMOLECULAR DYNAMICS OF HIGHLY VIBRATIONALLY EXCITED MOLECULES

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Direct studies of highly vibrationally excited polyatomic molecules with internal excitation energies comparable to the potential energy barriers for an intramolecular isomerization reaction or the dissociation of the molecule are of fundamental importance for our understanding of unimolecular elementary chemical reactions. The major topics which reveive central attention are, on the one hand, the elucidation of the dynamics of highly excited molecules in terms of the underlying potential hypersurfaces and, on the other hand, critical tests of the basic postulates and predictions of the statistical rate theories, which have been so successful for describing unimolecular reactions in thermal environments. At least for selected model systems, these fundamental questions are urging for exact investigations of the dynamics of the reactive species at chemically significant energies at a single vibration rotation quantum state resolved level of detail.

In our laboratory, we have performed new detailed state specific investigations of the spectroscopy and unimolecular dynamics of one particular system, namely the methoxy radical, CH_3O ($\tilde{X}$ ^2E), and its unimolecular decomposition according to

$$CH_3O\ (\tilde{X};\ E,\ J,\ \Gamma;\ v_i,\ K)\ \longrightarrow\ H + H_2CO. \qquad \Delta_r H_0^0 \approx 6\,900\ cm^{-1}$$

Using the technique of Stimulated Emission Pumping (SEP), we have been able to probe highly excited vibration rotation states of CH_3O ($\tilde{X}$) up to energies of $E_V \lesssim 10\,000\ cm^{-1}$, i.e. well above the asymptotic dissociation limit of the molecule [1]. The experiments were designed to address a number of specific topics:

a) Rotation vibration resolved spectra were recorded for the low energy regime of CH_3O and CD_3O to obtain a map of the potential surface for the molecules. Having resolved the rotational line structures, substantially different vibronic assignments had to be made for many levels than assumed before.

b) SEP scans for the high energy regime were considered at different experimental resolution to explore the intramolecular vibrational dynamics encoded in the spectra. First, in low resolution survey SEP spectra, a surprising persistence of vibrational structure was observed for energies above the dissociation limit of the molecule, despite of the usual notion of a "quasicontinuum" of states at these energies. Conclusions are evident pertaining to the short–time vibrational dynamics of the mole-

cules. Second, in high resolution scans over the coarse vibrational features, characteristic "clump" structures of individual vibration rotation eigenstates were revealed. These clumps are ascribed to distinctive optically active zero–order levels that are mixed with optically inactive "bath" states. Fourier transforms of the spectral autocorrelation functions have furnished information on the intramolecular vibrational redistribution (IVR) processes that would result after coherent ultrashort pulse excitation. IVR is observed to proceed on different time scales of between ≈ 0.3 and 2 ps [2].

c) High resolution linewidth measurements as well as investigations with direct time–resolved detection of the highly excited molecules at energies above the dissociation limit were carried out to measure the specific unimolecular dissociation rates for individual quantum states. These measurements reveal the existence of strong fluctuations of the lifetimes of single resonance states both in the tunneling regime below the classical dissociation potential threshold as well as in the normal unimolecular reaction regime above [2, 3]. The extent of these fluctuations can be related to the structure of the transition state for the reaction.

d) The rate constants for the collisional deactivation of excited single quantum states by noble gases were found to increase substantially with higher vibrational excitation. The inferred cross sections for the high energy regime exceed those for pure rotational transfer at low energies by a factor–of–two. Rotational and vibrational relaxation proceeds invariably simultaneously.

These unique, intimately related results are of general importance considering that the CH_3O system is large enough, as a five–atomic species with 9 vibrational degrees of freedom, that it presents a realistic model case for a simple bond fission reaction with far–reaching bearing to "typical" unimolecular reactions. In the talk, different aspects will be highlighted. Emphasis will be put in especially on the connection between the rates of IVR processes and the reactive lifetimes of individual resonance states of the molecules. Implications will be discussed for the unimolecular reaction dynamics of other systems under different conditions.

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High resolution spectroscopy of fragments from photodissociation

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Using multicolor laser experiments it became possible to put well specified photon energy into a molecule for dissociation and to observe the fragments in the different quantum states. The multiparametric study includes the variation of dissociation energy when probing a single fragment on a selected quantum state to obtain most detailed information on the dissociation channel. Three different examples of simple molecules, i.e. S_2Cl_2, SO_2 and TlI, will be given in this talk.

S_2Cl_2 is chosen because of its simple stucture (symmetry C_2) and of the possibility to study three particle dissociation S_2 and 2Cl which also could give new spectroscopic information on the radical S_2. The pump probe technique (i.e. dissociation-fragment detection) allows to split the absorption continua of S_2Cl_2 into the partial channels for state specific S_2. The spectra obtained showed the threshold for S_2 production and mark energy regions where only the fragmentation into S_2 and 2Cl is operating. S_2 is detected by the spectra in the wave length region 340-290 nm, the analogous system to the Schumann-Runge bands in O_2, yielding detailed information of the complex structure.

The second example is the photodissociation SO_2. The predissociating state C is chosen, to specify exactly the dissociating quantum state of SO_2 . SO is detected by the resonance enhanced photoionisation (REMPI) via the transition $A^3\Pi$- $X^3\Sigma^-$, and it was possible to follow the vibrational ladder of the A state up to its dissociation limit. The analysis of such spectra is simplified because SO is produced in a very small set of quantum states by the proper selection of the dissociation wavelength. Because of very precise setting of the wavelength for dissociation and of the sharp threshold behaviour, we found a dissociation wavelength where SO is produced only in the lowest vibrational and rotational state, i.e. a perfectly cooled molecule which is superb for further spectroscopie studies. On the other hand we will also demonstrate the obtainable simplification in the SO_2 spectroscopy by fixing the SO quantum state for probing.

In the third example we study the possibility to observe the transient state of a dissociating molecule with nanosecond pulse lasers. The diatomic molecule TlI is chosen to simplify the analysis of the new method. By applying strong laser fields the transition probability of a dissociating molecule at small internuclear distances (about 10 Å) is large enough to become

detectable. The spectra show broad and very asymmetric profiles which can be described by a curve crossing of repulsive states of a dressed molecule. Simulations with Landau-Zener approximation show that the difference potentials of the crossing states are derivable from the asymmetric structures. It will be discussed if this experimental method is able to study the coherent superposition of dissociating states produced by the laser pulse for dissociation.

FREE RADICALS IN INTERSTELLAR SPACE

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More than 80 different molecules (not including isotopic varieties) have been detected in interstellar space to date, a significant fraction of which are radicals. In this talk, we will first review the properties of the cold ($T \approx 10 - 50$ K), low density ($n(H_2) \approx 10^2 - 10^5$ cm^{-3}) interstellar clouds in which the radicals are found. Subsequently, the gas–phase molecular processes by which interstellar radicals are thought to be formed and destroyed will be discussed. These processes include:

Type	Process
	Formation Processes
Radiative association	$X + Y \rightarrow XY + h\nu$
	Destruction Processes
Photodissociation	$XY + h\nu \rightarrow X + Y$
Dissociative recombination	$XY^+ + e \rightarrow X + Y$
	Chemical Processes
Ion–molecule exchange	$X^+ + YZ \rightarrow XY^+ + Z$
Charge–transfer	$X^+ + YZ \rightarrow X + YZ^+$
Neutral–neutral	$X + YZ \rightarrow XY + Z$

Examples of each of these types of reactions involving interstellar radicals will be given, and the current knowledge of cross sections and reaction rate coefficients of each of the processes based on theory and experiment will be summarized.

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MICROWAVE SPECTRA AND STRUCTURE OF HC_3O

A.L. Cooksy, J.K.G. Watson, C.A. Gottlieb, and P. Thaddeus

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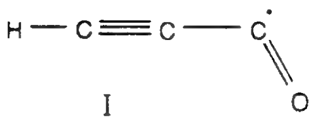
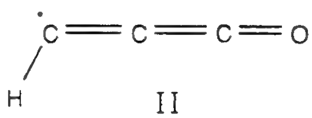
Carbon chains containing nitrogen or oxygen commonly exhibit quasilinearity. When such chains contain unpaired electrons, the dynamics of these molecules may become quite complex. Any quasi-linearity in HC_3O may be further complicated by the existence of two distinct geometries, probably separated by an extremely low isomerization barrier.





Using a millimeter-wave glow-discharge spectrometer, we have recently completed a comprehensive study of the rotational spectrum of the HC_3O radical, including isotopic substitutions at each atom and hyperfine measurements for all but the oxygen. The observed structure is essentially structure I, according to a preliminary analysis of the rotational constants. This conclusion is further supported by the Fermi-contact hyperfine constants of the three carbons, which decrease precipitously from 350 to 175 to 35 MHz with distance away from the oxygen atom, indicating the unpaired electron is strongly localized on the carbon atom adjacent to the oxygen. Previous *ab initio* calculations[1] find that structure II is also stable, but it is not detected in our discharge and is therefore at least a factor of four less abundant than the observed isomer. The interconversion between these two forms requires 40° changes in the CCH and CCO bond angles, and consequent rehybridization of the carbon molecular orbitals relatively small adjustments in an isomerization suggestive of a low barrier.

Spin-rotation perturbations between the $K_a = 0$ and 1 ladders, while hindering the initial assignment, have proven extremely valuable in the analysis, yielding accurate values for the $K_a = 0$–1 interval. Similarly, hyperfine perturbations among the spin-rotation components led to observation of the proton hyperfine splitting, which would otherwise be unobservable in the millimeter-wave transitions studied.

Two searches for HC_3O in the interstellar gas have been undertaken on the basis of the present laboratory work, one with the NRAO 30 m telescope, the other with the Nobeyama 43 m telescope. Both were unfortunately unsuccessful, but because both C_3O and HCCCHO have been detected in the molecular clouds, it is likely that HC_3O will be found when higher sensitivity observations are made.

1 Z.A. Tomasic and G.E. Scuseria, J. Phys. Chem., 95, 6905 (1991).

Rotational energy transfer of OH in collision with He, Ar or H_2

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Inelastic scattering of open shell diatomics has become a subject of considerable interest in current experimental and theoretical work on molecular dynamics. At the experimental side the fast development of efficient state selective laser detection techniques in combination with pulsed supersonic molecular beams has made possible the measurement of state-to-state cross sections for rotational energy transfer. Furthermore, efficient pulsed sources of free radical beams have become available making this field now also accessible for the study of scattering of chemically unstable species. A strong impetus to the progress of theory in this field has been given by the recent observations of weakly bound open shell van der Waals complexes which are nowadays one of the main topics in molecular spectroscopy. The spectroscopy of these van der Waals molecules as well as the dynamics of the collision process are governed by the same physical quantity, i.e. the potential describing the intermolecular interactions.

Of all the open shell species the OH molecule probably is the most frequently studied and consequently best understood free radical. As an intermediate species in many chemical reactions it plays a crucial role in various processes which are of fundamental importance like in combustion, plasmas, chemical vapour deposition and in the atmosphere. The study of the collision dynamics of OH is essential to understand and eventually control these processes. In the interstellar space the rotational energy transfer of OH by collisions with H_2 is one of the basic processes which are thought to be responsible for the observed anomalous Λ-doublet emissions from this molecule. Despite of its relevance the rotational energy transfer of OH in the electronic ground state $X^2\Pi$ has practically not been studied sofar.

For the determination of the intermolecular potential, which is the final goal of these studies, the most useful experimental quantities are state-to-state cross sections. In order to obtain these cross sections the OH molecules have to be prepared in a well defined quantum state. In the present study this is performed by rotational cooling in an expanding molecular jet, followed by electrostatic state selection. Hereafter about 95% of the OH radicals in the beam are in the upper $J = 3/2$, Λ-doublet state. These molecules collide with a secondary beam of Ar, He or H_2. The collision induced redistribution of the initial population is then probed by LIF detection. Without electrostatic state selection both $J = 3/2$, Λ-doublet states are initially populated. Combined with the scattering results for the upper Λ-doublet state the cross sections for the lower $J = 3/2$, Λ-doublet state are obtained.

Strongly different propensities are observed for the transitions to e- or f-states from the two $J = 3/2$, Λ-doublet states. These can be ascribed to quantum interference effects between the two potential surfaces $V_{A'}$ and $V_{A''}$ governing the collision process [1]. Quantum scattering calculations on the OH-Ar and OH-He systems have recently been carried out by Werner and coworkers [2]. The OH-Ar calculations are based on an *ab-initio* potential that was used also for the calculations of the bound energy states of the OH-Ar van der Waals complex [3]. The experimental results show a surprisingly good agreement with most of the calculated cross sections. However, also some deviations are observed, which seem to be related to imperfections in the difference potential $V_{A'}$-$V_{A''}$. For OH-H_2 the measured cross sections will be compared with new results from presently performed quantum scattering calculations of Clary and coworkers and of Offer, using two different *ab-initio* potentials.

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ROTATIONALLY AND ELECTRONICALLY INELASTIC SCATTERING OF DIATOMIC FREE RADICALS

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The simplest inelastic molecular collisional process, at least from the viewpoint of a theoretical treatment, is a rotationally inelastic process, in which the orbital motion of the molecule with respect to the collision partner couples with the rotational motion of the molecule through the anisotropy of the interaction potential. For a molecular free radical, the coupling of nuclear rotational angular momentum with the now nonzero electron spin and/or orbital angular momenta yields several fine-structure levels for each value of the total angular momentum. Thus, rotationally inelastic collisions can change the nuclear rotational momentum and/or the fine-structure levels of the molecular free radical. Recent advances in molecular beam and laser preparation and detection techniques have allowed the state-resolved study of rotationally and electronically inelastic collisions involving a number of open-shell diatomic electronic states. For the theoretical interpretation of such collisional processes, it has been possible not only to set up the framework for carrying quantum close coupled calculations of inelastic cross sections for specific systems but also to derive propensity rules governing the likelihood of certain types of fine-structure transitions. This talk will review a selected set of experimental and computational results which illustrate our present understanding of the dynamics of such processes, with particular emphasis on recent experiments carried out in our laboratory on the NH and CN free radicals.

DETERMINING BRIDGED STRUCTURES IN SMALL MOLECULES AND IONS FROM THEIR MILLIMETER WAVE SPECTRUM

Claire Demuynck
Laboratoire de Spectroscopie Hertzienne, Université de Lille, France

Millimeter wave spectroscopy is a very efficient tool for determining molecular structure. Its development has also been strongly motivated by the discovery of numerous species in space by radioastronomy. Among them, there is a special interest in neutral and ionic reactive species, due to their important role in the chemistry of the interstellar and circumstellar medium. Moreover, these reactive species often exhibit non conventional molecular structure related to the presence of non-saturated bonds, and thus are also of interest for quantum chemistry.

The main experimental problem is related to the low concentration of the reactive species in the absorption cell. These species are created in low pressure plasmas in various gas mixtures. Moreover, a very flexible, highly sensitive spectrometer, with a wide frequency range, has been developed.

Due to the mysterious chemistry which takes place in the absorption cell, the identification of the observed spectra is sometimes not straightforward. It relies on the behaviour of the observed signals versus various parameters, such as the discharge regime, the chemical composition of the gas mixture or the estimated lifetime of the molecule, and on the typical patterns which can be recognised in the spectrum. But this identification also depends critically on the available *ab initio* calculations which are in many cases the only source of information concerning the molecular structure of the species of interest.

In this talk, the experimental set up will be described, and the methods of identification of the spectra will be illustrated with some recent results obtained in silane and acetylene plasmas.

FOURIER-TRANSFORM MICROWAVE SPECTROSCOPY OF FREE RADICALS AND RADICAL COMPLEXES

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Pure rotational spectra of several free radicals and radical complexes were observed by a pulsed-discharge-nozzle (PDN) Fourier-transform microwave (FMTW) spectrometer. Pulsed beam FTMW spectroscopy with a Fabry-Perot cavity has been shown to have high sensitivity in the *cm*-wave region,[1] being extensively used to study molecular complexes. We have implemented a pulsed discharge nozzle to our FTMW spectrometer to produce short lived species in the free jet expansion.[2] As the spectrometer works in a low frequency region compared with other methods applied to study pure-rotational spectra of short lived species, it is particularly suited for species with small rotational constants. Furthermore, since the method produces short lived species in a supersonic free jet, it also enables us to study molecular complexes containing short lived species. Such a study is not possible by other methods using static absorption cells for the production of short lived species.

We have started a few projects with this PDN-FTMW spectrometer. One is the study of free radicals with a long carbon chain backbone. Such species are candidates of interstellar molecules, as number of molecules with a fairly long carbon chain have already been detected in interstellar space. Laboratory detection of new species is expected to have crucial importance to unveil the reaction mechanism why such long carbon chain molecules are abundant in interstellar space. So far, we were able to observe HC_4O, HC_3S, HC_4S, C_4S,[3] and C_5S. Detailed spectroscopic data for these species enable us to search them by radiotelescopes. Furthermore, we are able to discuss their electronic structures and linearities by comparing them with those of related spices with shorter carbon chains.

The second project is the observation of molecular ions. It has been considered that it is quite difficult to study rotational spectra of ionic species in the *cm*-wave region as the charged plasma has been thought to seriously disturb the microwave transmission. We found that molecular ions could be observed without serious disturbances. Species so far observed are HCO_2^+ and $HOCS^+$.

The third project is an application of the laser ablation method for the production of radical species containing metal atoms. We have detected MgCl in its ground $^2\Sigma^+$ state, where we were able to resolve its hyperfine structure for the first time.

The last project we are pursuing is the spectroscopic study of complexes containing short lived species. Spectra of Ar-CS, Ar-SO, and Ar-OH[4] have so far been detected. Many interesting features arising from large amplitude motions generally existing for such loosely

coupled molecular complexes have been observed and discussed.

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POTENTIAL ENERGY SURFACES FROM THE SPECTROSCOPY OF OPEN-SHELL AND CLOSED-SHELL VAN DER WAALS COMPLEXES

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Rotationally resolved spectra of Van der Waals complexes can provide a wealth of information on intermolecular forces, especially when several Van der Waals bending and stretching states can be observed. Over the last 5 years, we have used rotationally resolved far-infrared and mid-infrared spectra to obtain reliable potential energy surfaces for systems such as Ar–HF, Ar–HCl and Ar–HCCH. In the most favourable cases, such as Ar–HF and Ar–HCl, global potentials have been determined as a function of the intermolecular distance R, the intermolecular angle θ and the monomer vibrational quantum number v. These potentials have been found to be remarkably accurate in predicting new bands in the spectrum (usually within 0.1 cm−1) and in reproducing collisional properties such as inelastic differential cross sections and pressure broadening and shifting coefficients.

Recently, we have been extending this work in several ways. We have developed theoretical models for the spectra of complexes containing open-shell diatomic molecules, and have obtained new empirical intermolecular potentials for Ar–OH ($X2\Pi$) from the stimulated-emission pumping spectra of Lester and coworkers. We have investigated the energy level patterns in complexes containing open-shell atoms, such as Cl–HCl, and in complexes containing more complicated monomers, such as Ar–CH_4 and Ar–C_2H_4. We have also begun to obtain detailed information on non-additive (3-body) intermolecular forces in molecular systems, by performing calculations on the spectra of Van der Waals trimers such as Ar_2–HCl and Ar_2–HF.

Laser Induced Fluorescence Spectroscopy of Complexes Containing Free Radicals

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In the last few years the experimental challenges to studying complexes containing free radicals have begun to be overcome. The rewards for this progress are considerable. The open-shell nature of one moiety enhances the possibility for incipient chemical as well as the usual physical (van der Waals) bond formation in these species. While the spectra are more complex due to fine and hyperfine structure interactions, ultimately they are more informative because of the presence of these additional molecular probes. We have examined a number of inert-gas radical containing complexes: *(i)* hydride complexes, Ar•OH, Ne•OH, and Ar•SH; *(ii)* cyclopentadienyl and methylcyclopentadienyl (MeCp) complexes: Cp•He, Cp•He_2, Cp•Ne, and MeCp•He_2; and *(iii)* $CdCH_3$ complexes: He•$CdCH_3$, Ne•$CdCH_3$, Ar•$CdCH_3$, Kr•$CdCH_3$ and Xe•$CdCH_3$. In all cases, except for the heavier $CdCH_3$ complexes, we have performed high resolution work with our 100 MHz resolution laser induced fluorescence system. This work is particularly valuable because it alone reveals all the fine and hyperfine structure probes inherent in these open-shell spectra. The details of a number of our findings will be discussed.

INFRARED SPECTROSCOPY OF TRANSIENT MOLECULES

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The study of the vibration-rotation spectra of unstable species recorded with a Fourier transform interferometer requires specific procedures. We describe some of the methods which have been developped in our laboratory to produce, detect, record and analyse spectra of transient molecules.

New experimental developments on time-resolved wideband spectroscopy are also given.

NEAR-INFRARED FOURIER-TRANSFORM EMISSION SPECTROSCOPY ON FREE RADICALS

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Emission spectra of transitions from low-lying metastable electronic states of diatomic radicals have been studied in the NIR region with high-resolution BOMEM or BRUKER FT spectrometers. The radicals were produced and excited by chemical reactions and energy transfer processes in fast-flow systems. Different groups of radicals and types of transitions have been studied,

- $a^1\Delta_{(g)} \rightarrow X^3\Sigma^-_{(g)}$ and $b^1\Sigma^+_{(g)} \rightarrow X^3\Sigma^-_{(g)}$ transitions of radicals of the O_2/NF family,
- $a^3\Sigma^-_{(u)}(a_1 1^{\pm}_{(u)}) \rightarrow X^1\Sigma^+_{(g)}(X0^+_{(g)})$ transitions of group VA diatomics (Bi_2, BiN, Sb_2),
- transitions between the fine structure components of widely split $X^2\Pi$ or $X^3\Sigma$ ground states of metal hydrides, halides and chalcogenides (BiH, BiX, BiY, TeH, TeX, PbX; X=F,Cl,Br,I; Y=O,S,Se),
- continuous emission of collision complexes near weak magnetic dipole or electric quadrupole transitions (O_2^*:M b→a and a→X, N^*:Xe $^2P \rightarrow {}^2D$).

For a number of radicals, analysis of high-resolution spectra has yielded accurate molecular constants for the ground state and low-lying excited states including hyperfine interaction constants. In the $b^1\Sigma^+ \rightarrow X^3\Sigma^-$ bands of SO and SeS, weak magnetic dipole branches have been observed in addition to the much stronger electric dipole branches. Analysis of the relative line intensities, together with lifetime measurements of the b states, allowed determination of the electric and magnetic transition dipole moments μ_0, μ_1, and M.

The emission spectrum of BiO radicals excited in the reaction system of Bi_x vapour with microwave-discharged oxygen was studied in the range 6000-31000 cm^{-1}. Seven new electronic states and

15 new transitions have been observed and partly analysed. With the help of detailed quantum-mechanical MRD-CI calculations of Buenker et al.[1], all known valence states of BiO can be assigned to the spin-orbit states arising from low-energy electron configurations.

Pulsed laser techniques (LIF, ELP) have been used to study the radiative lifetimes and quenching rate constants of the upper spin-orbit components $X_2{}^2\Pi_{3/2}$ (BiO, BiX) and $X_2 1^{\pm}$ (BiX). The radiative lifetimes are found to lie in the range 0.5-20 ms. Very high rate constants have been measured for near-resonant E-E and E-V energy transfer processes involving the spin-orbit transitions of BiO and PbF.

Medium-resolution measurements with a FT spectrometer have been used to study the collision-induced broad band emission underlying the discrete rotational lines of the $a^1\Delta_g \rightarrow X^3\Sigma^-{}_g$ and $b^1\Sigma^+{}_g \rightarrow a^1\Delta_g$ transitions of molecular oxygen. The rate constants for the two collision-induced processes were found to be correlated and proportional to the polarisibility of the collision partner. The results strongly support the mechanism of collision-induced emission and absorption in the b↔a and a↔X bands of O_2 suggested by Minaev[2]. It is concluded that this mechanism also determines the radiative decay rates of $O_2(a^1\Delta_g)$ in matrices and in solutions.

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RADICALS AND IONS IN PLASMAS USED FOR SEMICONDUCTOR PROCESSING

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Free radicals play a major role in the chemistry of plasmas used for a variety of industrial processes such as semiconductor etching, plasma nitriding, and polymer treatment and formation. Detection of these reactive species inside plasma chambers in a non-invasive fashion can be carried out by a variety of optical methods, and this talk will describe our recent work using laser induced fluorescence (LIF) to detect a number of species, particularly those involved in plasmas of fluorinated hydrocarbons used for the etching of Si and SiO_2 surfaces.

Chemical modelling of plasmas requires measurements of the concentration of reactive species - atoms, radicals, ions and electrons - spatially resolved if possible, together with information on their production rates, reaction rates and interactions with the substrate surface. In a plasma of CF_4, the CF and CF_2 radicals are the most important polyatomic species, and their concentrations, internal energy distributions (giving an idea of the plasma 'temperatures'), spatial distributions, and rates of loss on the substrate have been measured using standard LIF techniques. CF_4/O_2 mixtures have been long used in etching processes, and measurements of O atom concentrations, by two photon LIF at 226nm, has been used to follow the chemistry of O atoms in this complex mixture. Amplified spontaneous emission accompanies LIF in these high laser intensity driven processes and reveals Doppler narrowed resolution of the two photon transitions.

Although ions are present in lower concentrations than radicals in most processing plasmas, LIF can be used to detect them and to infer their behaviour in the strong DC fields, particularly those near the plasma sheath region close to the substrate surfaces. Increasingly a knowledge of the kinetic energy distributions of the ions is required in order to understand ion-surface treatment processes using plasmas, and in principle Doppler lineshape profiles in LIF can achieve this, and also reveal the anisotropic nature of the ions' velocity distributions. Results on the lineshape measurements of N_2^+ in a simple RF parallel plate reactor will be described.

MICROSCOPIC AND MACROSCOPIC DYNAMICS OF FREE RADICALS IN COMBUSTION

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Experimental possibilities for studying radical reactions in detail have expanded quite dramatically in recent years as the result of the development of various laser sources with high temporal, spectral and spatial resolution. In addition to illuminating microscopic details of the elementary reactions taking place in combustion processes in situ detection of the free radicals is specially important in the effort to improve fuel efficiency and reduce emission levels in practical combustion devices.

1. Microscopic Dynamics of Elementary Reactions

The results of experiments on the microscopic dynamics of the reactions of hydrogens atoms and hydroxyl radicals with O_2, CO, OH_2, CO_2, H_2O relevant in combustion and atmospheric chemistry using four wave mixing process to generate tunable L-α radiation for the sensitive detection of hydrogen atoms are compared with classical and quantum predictions.

2. Reduction of NOx Emission in Municipal Waste Incinerators by Free Radical Reaction

The selective reduction of NO in the presence of O_2 by free radical reactions was studies in a plug-flow reactor using tunable diode laser spectroscopy. Addition of small amounts of hydrocarbons increases radical chain reactions so that the reaction with NO takes place at lower temperature and the noncatalytic reduction of NO in a waste incinerator could be realized under normal operating conditions.

3. Quantitative Detections of OH Radicals in large Scale Premixed Natural Gas Flames

2D- and 3D- saturated LIF of OH radicals with simultaneous 2D-UV-Rayleigh-thermometry and 2D-PIV was used to analyse highly turbulent premixed natural gas flames. Profiles of OH concentrations and temperatures normal to the flame front showed good agreement with flamelet predictions even at large turbulent Reynolds numbers. The laser technique was also applied to domestic natural gas heating systems, where temperature and NO concentration fields could be determined to optimize the burner geometry for low NO_x emissions.

4. Ignition and Knock in Otto-Engines

Spatial and temporal resolved temperature distributions were obtained by 2-line 2D-OH-LIF during the ignition of CH_3OH /O_2 mixtures. Preheating of the gas mixture significantly accelerates the burning velocity in this region so that the development of knock phenomena can be explained by mathematical modelling.

SPECTROSCOPY AND DYNAMICS OF SMALL IONIC COMPLEXES

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The spectroscopic and dynamical properties of small gas phase cluster ions, consisting of a *molecular* ion core surrounded by one or more rare gas atom ligands, are discussed. Using a combination of mass spectroscopic and laser techniques it is possible to selectively prepare and characterise species such as N_2^+-He_n and N_2O-Ar^+ and observe how various properties develop as successive ligand atoms are added. In the past, the generation of sufficient densities of cold ionic complexes with specific constitution has been an obstacle. Employing a hybrid electron impact supersonic expansion ion source it has proved feasible to generate useful currents of cluster ions with internal temperatures of less ≈30 K.

In one series of experiments, heteroclusters consisting of an N_2^+ cation surrounded by helium [1] and neon solvent [2] atoms have been studied. Usually the strong B←X electronic transition of the N_2^+ chromophore (occurring at ≈390 nm) has been exploited to excite the complex and photoabsorption has been inferred by monitoring the appearance of N_2^+ fragments. For both N_2^+-He_n and N_2^+-Ne_n the positive charge (hole) is primarily localised on one component (the N_2 molecule). Analysis of the electronic spectra suggests that N_2^+-He is quite floppy in the angular coordinate in both X and B electronic states with very little change (<1 cm^{-1}) in the He···N_2^+ interaction well depth accompanying electronic excitation. The N_2^+-Ne species on the other hand appears to be quasi linear at lower internal energies but becomes unbound in the angular coordinate as the internal energy increases.

Other experiments have focused on the dynamics of N_2^+-He_n and $(N_2)_n^+$ cluster fragmentation. By measuring the time dependence of hot band intensities it has proved possible to determine vibrational predissociation/vibrational relaxation rates for N_2^+-He_n complexes that possess quantum of the N-N stretch vibration[3]. As expected, the relaxation rate increases with ligand number (from 4.5 10^3 s^{-1} for N_2^+-He to $2.0 \cdot 10^4$ s^{-1} for N_2^+-He_6) though the rate appears to approach saturation before completion of the first solvation sphere.

The smaller $(N_2)_n^+$ clusters (n<7) photofragment to yield either N_2^+ or N_4^+ fragments when exposed to light in the near UV. By conducting the photolysis in an argon buffer gas, the extreme sensitivity of the $N_2^+(\upsilon=n)+Ar \rightarrow N_2+Ar^+$ charge transfer reaction (where the cross section increases by two orders of magnitude when going from $\upsilon=0$ to $\upsilon=1$ [4]) can be exploited to determine the degree of fragment N_2^+ vibrational excitation and hence explore the energy partitioning accompanying cluster fragmentation. A decrease in N_2^+ fragment

vibrational energy as the clusters become larger is consistent with the occurrence of efficient intracluster charge and vibrational energy transfer.

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Rotationally resolved resonance enhanced multiphoton ionization photoelectron spectroscopy of OH and NH

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Resonance enhanced multiphoton ionization in combination with kinetic-energy-resolved photoelectron spectroscopy (REMPI-PES) is a highly selective and sensitive tool for the detailed study of excited states of small molecules. In contrast to ion detection, where only the *presence* of ions is detected, an important advantage of electron detection is that additional information is obtained on ion *internal energies*. When diatomic hydride radicals such as OH and NH are studied, their relatively large rotational constants allow the measurement of photoelectron spectra in which not only separate electronic and vibrational levels can be distinguished, but with a resolution even down to the rotational level. The accurate determination of ionic branching ratios is important, because they provide an effective means of getting at the fundamental processes which lie at the root of photoionization dynamics. In these processes angular momentum plays a central role, and hence reliable and detailed experimental information about angular momentum associated with *rotation* is very valuable.

The OH radical is produced through photodissociation of hydrogen peroxide (H_2O_2). In our experiments OH is predominantly generated in its electronic ($X\ ^2\Pi$) and vibrational (v''=0) ground state, but with an appreciable degree of translational and rotational excitation. Rotationally resolved photoelectron spectra of the OH radical in all its populated rotational levels associated with the Rydberg D $^2\Sigma^-$ (v'=0-2) and 3 $^2\Sigma^-$ (v'=0) states can be obtained. Sophisticated *ab initio* calculations have been performed and show generally good agreement with experimental rotational branching ratios. The results are a clear illustration of the significant influence that Cooper minima in specific photoionization channels can exert on the rotational ion distributions. Moreover, effects of the strongly anisotropic molecular field and of orbital evolution should be incorporated [1,2].

The NH radical is produced through photodissociation of hydrazoic acid (HN_3). The NH radical is generated almost exclusively in its metastable a $^1\Delta$ electronic state, rather than in its X $^3\Sigma^-$ ground state. Both these states derive from the same electronic configuration $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^2$. The excess kinetic energy on photofragmentation goes into translational, vibrational, and relatively little rotational excitation. A multitude of excited states arising from excitation of a 1π electron into a molecular Rydberg orbital is observed. In view of the above we shall be solely concerned with Rydberg states which belong to the *singlet* manifold. We shall consider Rydberg states belonging to the 3p complex, *viz.*, in the order of increasing energy, f $^1\Pi$, g $^1\Delta$, and h

$^1\Sigma^+$. Also, states which are part of the 3d complex, *viz.*, i $^1\Pi$ and j $^1\Delta$ will receive attention. Finally, the valence excited d $^1\Sigma^+$ state has also been studied in detail. Photoelectron spectra, often rotationally resolved, of all of the above excited states have been observed. Comparison with the results of *ab initio* calculations again illustrates the importance of Cooper minima, and the role played by orbital evolution and the anisotropy of the molecular field [3,4]. In addition, REMPI-PES proves to be an invaluable tool for obtaining detailed information about the degree of configuration interaction present in molecular excited states. Such information is generally difficult to obtain by other experimental means [5] .

Photofragmentation of hydrazoic acid does not terminate at the generation of the NH radical. Subsequently, this diatomic hydride can be photodissociated into atomic fragments, with N atoms produced in their metastable $^2D^o{}_J$ and $^2P^o{}_J$ states, rather than in their $^4S^o{}_{3/2}$ ground state. With these metastable states as a starting point, extensive hitherto unobserved *np* and *nf* Rydberg series of atomic nitrogen have been identified using REMPI-PES. Core- and non-core-preserving transitions to ionic states, and in one case almost complete state selection to an excited state of the nitrogen ion are observed [6].

In recent years many research groups have devoted much effort towards achieving state-selective chemistry. REMPI-PES studies have shown that atomic and molecular cations can be generated selectively in specific quantum states, when ionization takes place via suitable excited states. The development of effective REMPI-PES strategies of how to produce state-selected ions, even down to the molecular rotational level, and their subsequent use in ion-molecule reactions, could well prove to be instrumental in the future realization of what are still the dreams of present-day chemists.

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STRUCTURE, REACTIVITY AND DYNAMICS FOR SMALL METAL CLUSTERS

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Small metal clusters, particularly transition metal clusters, provide a fascinating opportunity to view the detailed dynamics of reactions occurring at multiple metal centres. Indeed, properly developed, this field could provide an alternative system of models for surface reactions to that provided by single crystal substrates. However, there are formidable obstacles to overcome as, as yet, we know few structures for transition metal clusters and no structures for ligands adsorbed at the surface of such structures.

In this talk, I will review structure/reactivity relationships in such systems. I will discuss high and low resolution spectroscopic methods for investigating transition metal clusters and present recent results for gold clusters with 6, 7, 8, 9, 10, 11, 12 and 13 valence electrons. In addition, I will present a detailed description of a novel *statistical* molecular ionization process which we have observed for the first time in small niobium, tantalum and tungsten clusters. It will be shown that this ionization is governed by a statistical rate process and that this rate can be used to establish a thermometry for metal cluster beams.

THE ONSET OF CHAOTIC BEHAVIOUR IN THE ELECTRONIC SPECTRA OF DIATOMIC 3d METAL COMPOUNDS

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An understanding of the spectra of metal-containing radicals can be achieved by combining results from supersonic jet-cooled laser-induced fluorescence experiments with other high resolution techniques such as intracavity laser or intermodulated fluorescence. In this way survey spectra can be taken over wide wavelength ranges, and the details of the rotational and hyperfine structures of individual bands elucidated. Recent results for the diatomic 3d oxides and nitrides show that the spectra can be well understood using the single configuration approximation for the early members of the series, while spectra from the later members (such as iron and cobalt) are increasingly complex. For example, spectra of VO are formidable because of the quartet multiplicity and the I=7/2 nuclear hyperfine effects, but can be understood in quantitative detail: an example is the ($B^4\Pi$, $a^2\Sigma^+$) - $X^4\Sigma^-$ system where the details of the hyperfine structure at the electronic perturbations can be fitted with an r.m.s. error of 15 MHz. On the other hand FeO and CoO have so many more electronic states that interpretation is difficult. CoO is a case in point.. There are over 100 bands in the region 750 - 430 nm coming from $X^4\Delta_{7/2}$, v = 0 alone; at the long wavelength end they can be arranged into progressions and assigned to configurations from their hyperfine structures, but at the short wavelength end there are no easily-recognized patterns.

POSTER SESSION A

Monday 6 September 1993
14.00 u

REACTION DYNAMICS OF $O(^3P, ^1D)$ AND $Cl(^2P)$ ATOMS AND $OH(^2\Pi)$ RADICALS WITH SIMPLE MOLECULES IN CROSSED BEAMS

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In our laboratory we have recently undertaken the study of the reaction dynamics of ground, ^3P, and electronically excited, ^1D, oxygen atoms with simple molecules by using the crossed molecular beam scattering method with mass spectrometric detection. We exploit the capability to generate intense and continuous supersonic beams containing both $O(^3P)$ and $O(^1D)$ by radio-frequency (RF) discharge in O_2/rare gas mixtures at high pressure and at high RF power. The first reactions we have looked at are those with hydrogen halides, relatively to H-displacement channel, which are strongly endoergic for $O(^3P)$ while exoergic for $O(^1D)$ [1,2]. Reactions which are exoergic for both $O(^3P)$ and $O(^1D)$, as those with H_2S, have also been investigated [2,3]. From high-resolution product angular and velocity distribution measurements at different collision energies product velocity flux contour maps in the center-of-mass frame are derived. The variation of the reaction dynamics of $O(^1D)$ along the HX series is examined. With the study of the reactions with H_2S the effect of electronic excitation on the reaction dynamics of atomic oxygen is assessed under the same experimental conditions.

More recently we have adapted the same RF discharge beam source for the generation of a supersonic beam of OH radicals, starting from dilute mixtures of water in He (or He/Ne). This has permitted us to carry out crossed beam studies of the dynamics of the reaction $OH + D_2$ [4] and OH + CO [5] of great importance in combustion and atmospheric chemistry. Comparison with related experimental and theoretical work have also been carried out [4,5].

In the last few months the same RF discharge beam source has also been adapted for the generation of chlorine atoms starting from mixtures of Cl_2 in He. Preliminary results on the reactions $Cl + H_2$ and $Cl + D_2$ have been obtained.

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The observation and analysis of the far infrared laser magnetic resonance spectrum of the HSS Radical

S.H. Ashworth, K.M. Evenson and J.M. Brown

While recording the far-infrared laser magnetic resonance (LMR) spectrum of the SH radical[1] in 1991 a spectrum of another species was observed. The species was obviously heavier, quite possibly the HS_2 radical. The same spectrum could be observed using either the reaction of hydrogen atoms and elemental sulphur or fluorine atoms and hydrogen sulphide. Addition of oxygen produced very different signals attributable to SO and HSO.

More recently we have recorded more of the far-infrared LMR spectrum of the HS_2 radical. The spectrum has been found, as expected, to be dense and complex. Transitions in a number of K sub-bands have been recorded but, as yet, only a few have been assigned. The chemistry producing the spectrum is consistent with HS_2 formation and is very sensitive to the addition of impurities such as nitrogen or oxygen. The latter produces an entirely different spectrum which has been attributed to the HSO radical.

The reaction of fluorine atoms and hydrogen sulphide used to produce the radical in the sample region occurs at very low pressure and in many cases the proton hyperfine structure is almost completely resolved.

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ERROR ANALYSIS FOR COMPLEX KINETICS SYSTEM METHYL-VINYL CROSS RADICAL REACTIONS

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Tunable Far Infrared (TuFIR) Spectroscopy of the Chlorine Monoxide, Hydroperoxy and Formyl Radicals.

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We report the observation of high resolution, ground state pure rotational transitions of three transient species important in atmospheric and combustion studies: ClO, HO_2 and HCO by Tunable Far Infrared (TuFIR) spectroscopy.

The generation of TuFIR laser sidebands have been achieved by non-linear mixing of radiation from a fixed frequency FIR laser and a tunable microwave source. The TuFIR sideband spectrometer incorporates the use of an optically pumped FIR laser as the local oscillator (LO) and a reflex klystron of centre frequency 90 GHz as the tunable microwave source, providing sidebands of the LO after mixing on a GaAs Schottky Barrier Diode *ie.* $\omega_{TuFIR} = \omega_{FIR} \pm \omega_M$. Hence the tunability of the TuFIR sideband is determined by the microwave frequency, ω_M. Following the necessary filtering and separation of the sideband from the FIR 'carrier' frequency, a double-pass of the absorption cell is achieved and the resulting signal is recovered via phase sensitive detection.

The ClO radical was formed by a microwave discharge in a mixture of chlorine and oxygen and the products pumped through the absorption cell. The Λ–doubled J = 17.5 -16.5 transition in the $^2\Pi_{3/2}$ ground state of ^{35}ClO was obtained with a S:N ratio of > 100:1. The HO_2 radical formed by mixing O_2 and CH_3OH with the products of a microwave discharge in Cl_2/Ar in a fast flow system . Proton hyperfine structure in, for example, the $10_{1,9}$ - $10_{0,10}$ transition of the X^2A'' state at 625.661 and 625.664 GHz was easily resolvable. Pressure broadening analysis of both the ClO and HO_2 observed atmospherically has been accomplished.

The HCO radical has been successfully generated by various methods for example, the reaction between formaldehyde vapour and the products of a microwave discharge in CF_4/Ar. The strong a-dipole $10_{1,10}$ - $9_{1,9}$ fine structure components in the ground $^2A'$ state are within the range of the spectrometer (600 -1000 GHz) and can clearly be observed.

EXTENDING INFRARED KINETIC SPECTROSCOPY

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Infrared kinetic spectroscopy is being extended by the development of methods for measuring the rate constants of new classes of reactions over extended temperature ranges, by the development of a new widely tunable infrared source, and by the combination of radical preparation by flash photolysis with cold slit jet transient infrared absorption. The recombination rate of propargyl radical has been measured as 1.8(4) x 10^{-10} cm^3sec^{-1} at 296K through calibration of the infrared absorption cross-section of propargyl radical against the infrared Br atom signal produced simultaneously upon photolysis of propargyl bromide. The pseudo first order method for measuring rate constants has been extended at 296K to the atom-free radical system, NH_2+O. The channel producing OH + NH has been found to be unobservably small. The rates of the reactions, NH_2+O, and O + HNO (HNO is from the NH_2+O channel, H + HNO) have been measured. The rate of the reaction C_2H + H_2 has been measured in the temperature range 295-875 K. IRKS results are now being produced with the new widely tunable infrared source based on difference frequency generation in $AgGaS_2$ in the form of the high resolution spectrum of ν_2 band of HCCN. It has been established that larger radical species can be observed in pulsed slit jet flash photolysis transient infrared absorption spectroscopy through the observation of ν_1 of propargyl radical.

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Resonant two-photon ionization (R2PI) spectroscopy on transition metal dimers: Cu_2, Ti_2 and Zr_2.

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Using the R2PI technique on beams containing clusters of transitions metals produced by laser ablation we have studied the spectra of Cu_2, Ti_2 and Zr_2. The latter two observed for the first time. A time-of-flight mass spectrometer used in reflectron arrangement and equipped with a channel-plate detector mass-selected not only the dimers but also the different isotopomers. This technique also offers unique possibilities to study lifetimes of the excited states almost free from the common errors.

For the copper dimer the A-X system was studied and some anomalies in the internuclear distances' variation with the vibrational quantum number due to interaction with an ionic state was treated. Lifetimes were measured for the A, B and C states and the results were found to be in accordance with this interpretation.

Two electronic transitions were observed for Ti_2 in the infrared region and it was necessary to Raman-shift the dye-laser output. The two transitions were observed at 953.5 and 1099 nm and the short wavelength system which is the strongest of them was analysed and found to be a $^3\Pi_{0u}$-$X^3\Delta_{1g}$ transition. Due to the low rotational temperature observed, 15 K, there is no doubt that the lower state of the observed spectrum is the ground state of the titanium dimer. This result is in accordance with theoretical prediction by Bauschlisher *et al.*[1]

In contrast to the titanium dimer the zirconium dimer showed a great number of bands - around 50 - in the near infrared (870 - 1020 nm). Attempts to analyse some of them indicate that the ground state probably has a $^1\Sigma$ character.

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MASS SPECTROGRAPHIC METHOD OF STUDY OF PRODUCTS OF DISINTEGRATION OF CHARGED MICRO DROPLETS

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Ion's hydration is a very important stage of the liquid phase reactions: determining a mobility of ions hydration influences the rate of the corresponding reactions. Several years ago we have developed mass spectrograph method of field evaporation of ions out of solutions (FEIS) for study of the hydration of positive ions in aqueous solutions.

The present report describes the similar experiments with negative halogen ions. The FEIS is a direct method for study of ion's hydration. It is distinguished from previous methods of study of ion's hydration with absence of anything assumptions about mechanisms of indirection between ions and water molecules. The FEIS method is based on the Rayleigh ruptures of the charged surface of an aqueous electrolyte solution. This ruptures must occur along the surfaces of the weakest interactions between stable aggregations of the solution. We consider the ionic clusters forming at this ruptures are the same stable aggregations. The hydration numbers for ions of F (2), Cl (2), Br (1.5) and J (1) are determined by the FEIS. The values of these numbers are in good coincidence with the ones determined by the previous methods using ion's motion.

Financial support was provided by Russian Fundamental Research Foundation grant 93-03-4933 (to I.I.Morozov).

The Fourier Transform Infrared Spectrum of Fluorine Cyanides

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High-resolution (0.0026 cm^{-1}) spectra of fluorine cyanides have been studied in the 2000-4700 cm^{-1} region using the Bruker IFS 120 HR spectrometer. The absorption path length in the white-type cell used was 104 meters at room temperature. Different runs with pressures of 1, 0.065 and 0.025 torr were needed.

The sample of FCN used in these studies was prepared by pyrolysis of cyanuric fluoride $(FCN)_3$ at 1400 °C in a graphite furnace under a high vaccum. Fifty three bands of $F^{12}CN^{14}$, ten of $F^{13}CN^{14}$ and five of $F^{12}C^{15}N$ have been analyzed. Some impurities have been detected (CF_4, C_2N_2, CO_2). Besides these impurities twenty six unknown bands have been detected. They present B values between 0.3635034 and 0.3680441 cm^{-1}. These bands are fading out with time and disappear after a few hours suggesting an unstable species. The ground-state rotational constant obtained from the analysis of these bands was $B_0 = 0.3666129(23)$ cm^{-1} which can be compared to the value of 0.3629cm^{-1} proposed by Botschwina et al.[1] for the isocyanide FNC. The fundamental vibration frequencies of FNC estimated from some transitions in this study are : $\nu_1(FN) = 1040$ cm^{-1}, $\nu_2 = 140$ cm^{-1} and $\nu_3(CN) = 2250$ cm^{-1}. In the case of FCN, in addition to the Fermi resonance between ν_1 and $2\nu_2$, $2\nu_1$ and ν_3, we have detected a fourth-order anharmonic resonance between $3\nu_1$ and $2\nu_2 + \nu_3$.

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ELEMENTARY REACTION OF $CHF(\tilde{X})$ AND $CF_2(\tilde{X})$ RADICALS WITH OZONE

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The electronic ground state of the fluorinated carbenes are singlett states in contrast to the triplett electronic ground state of the simplest carbene $CH_2(\tilde{X})$. A significantly different reactivity for $CH_2(\tilde{X})$ and $CHF(\tilde{X})$ respectively $CF_2(\tilde{X})$ can be expected. Therefore is of principal interest to study $CH_xF_y(\tilde{X})$ carbene reactions in order to find a correlation between electronic structure and reactivity. The reactions of $CHF(\tilde{X})$ and $CF_2(\tilde{X})$, in particular with ozone, are interesting from another point of view, since they are important for the understanding of the photochemistry of the polluted urban atmosphere.

The reaction of $CHF(\tilde{X})$ and $CF_2(\tilde{X})$ with O_3 were studied in an isothermal flow reactor in the temperature range ($403 \leq T/K \leq 573$) at a pressure of 2 mbar with He as the main carrier gas. $CF_2(\tilde{X})$ was produced in a microwave discharge of CF_2Br_2 diluted with He. The chemical reaction CH_3F + F atoms was applied as the $CHF(\tilde{X})$ source. $CHF(\tilde{X})$ and $CF_2(\tilde{X})$ were detected by laser induced fluorescence (LIF). The ozone was produced in an O_2 discharge and separated from O_2 and stored in a dry ice silicagel trap. The absolute O_3 concentration was determined via UV-absorption in a absorption cell connected to the flow reactor. Pseudo first-order rate constants were obtained under the experimental conditions $\{[CHF]_0, [CF_2]_0\} << [O_3]_0$.

For the reaction:

$$CHF(\tilde{X}) + O_3 \longrightarrow \text{products} \qquad (1)$$

a negative temperature dependence of the rate constant was observed $k_1(T) = 6.4 \cdot 10^{12}\ (T/298\ K)^{-0.5}\ cm^3/mol \cdot s$ in the above given temperature range. For the reaction:

$$CF_2(\tilde{X}) + O_3 \longrightarrow \text{products} \qquad (2)$$

a rate constant increasing with temperature was obtained, which can be described by the Arrhenius expression $k_2(T) = 3.9 \cdot 10^{12}\ \exp\ (-(27 \pm 8)\ kJ\ mol^{-1}/RT)\ cm^3/mol \cdot s$. These rate constants show that $CF_2(\tilde{X})$ is significantly less reactive towards oxidation than $CHF(\tilde{X})$. The same reactivity change was observed in other reactions e.g. towards olefines, in addition reactions to the double bonds of the olefines. Both fluorinated carbenes are in the gas phase less reactive than $CH_2(\tilde{X})$.

The products of reaction (1) and (2) can be assumed to be $CHFO + O_2$ and $CF_2O + O_2$ respectively. The spin conservation would lead to O_2 molecules in the singulett state. The reaction mechanisms will be discussed.

The CH_3 $3p_z$ $^2A_2''$–$\tilde{X}^2A_2''$ 0_0^0 band at temperatures up to 1700 K investigated by REMPI spectroscopy

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The 0_0^0 band of the CH_3 $3p_z$ $^2A_2''$ – $\tilde{X}$ $^2A_2''$ Rydberg transition has been recorded using REMPI spectroscopy. CH_3 was generated in a discharge flow reactor at room temperature and in a hot-filament-assisted chemical vapor deposition reactor (HFCVD) at temperatures of 700 K to 1700 K. By means of spectral simulation the rotational constants, B'and C', and the homogeneous and heterogeneous predissociation rates of the vibrationless $3p_z$ $^2A_2''$ state were determined. On basis of these spectroscopic constants and the well-known rotational and vibrational ground state constants, relative intensities of the CH_3 REMPI spectra were calculated for temperatures up to 2000 K. These spectra were used to evaluate relative CH_3 concentrations from measured REMPI peak intensities of the dominant Q branch. The production of a CH_3 reference concentration in the discharge flow reactor enabled absolute CH_3 concentration measurements in the HFCVD reactor using REMPI spectroscopy.

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MILLIMETERWAVE SPECTRUM OF HALOGENOFLUOROACETYLENES PRODUCED IN A DISCHARGE CELL

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Fluoroacetylenes belong to those compounds which are difficult to be synthesized by conventional chemical methods. In 1978 Bieri et al.[1] reported that fluoroacetylenes could conveniently be prepared by discharging through fluorine-containing aromatic compounds. Since then it became possible to conduct spectroscopic investigations of fluoroacetylenes.[2] Recently we have constructed a source-modulated spectrometer with a free space discharge cell. The spectrometer is controlled with a microcomputer. The frequency region below 100 GHz was covered with klystrons and higher frequency millimeterwaves (above 200 GHz) were obtained by using a frequency tripler. Halogenofluoroacetylenes XCCF (X = Cl, Br, and I) were prepared by glow-discharge through pentafluorohalogenobenzene (C_6F_5X) directly in the discharge cell.[3] We observed the microwave spectrum of halogenofluoroacetylenes in a few vibrationally excited states as well as in the ground state. The spectrum observed in the frequency range of 60 - 220 GHz was analyzed with a least-squares fit using a standard Hamiltonian. The molecular parameters including the rotational and centrifugal distortion constants, the l-type doubling constant, and the nuclear quadrupole coupling constant of X nucleus have precisely been determined. The rotational and centrifugal distortion constants of ICCF in the ground state are 1200.590266(77) MHz and 50.5314(54) Hz, respectively. We discuss the π and ionic character in ICCF on the basis of the iodine nuclear coupling constant.

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THEORETICAL STUDY OF THE C_2P RADICAL

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An ab initio study of the C_2P radical has been carried out. Two isomers were found to lie very close in energy: a linear CCP structure ($^2\Pi$ electronic state) and a cyclic (C_{2v} symmetry) isomer with a $^2B_2$ electronic state. Correlated calculations show the former to lie slightly lower than the latter, about 5 kcal/mol at the fourth-order Møller-Plesset level of theory. Predicitons of the geometries, vibrational frequencies and IR intensities, at the second-order Møller-Plesset level, have been made for both isomersin order to aid in their possible experimental detection.

We have also studied the C_2P^+ cation. Both isomers, linear and cyclic, have closed-shell electronic states, the linear CCP^+ structure lying about 15 kcal/mol lower in energy than the cyclic one. The estimated ionization potential for ground state CCP is 8.4 eV at correlated levels.

Calculations for the protonated structures $(C_2PH)^+$ have been carried out in order to estimate the proton affinity of this species, which is found to be relatively high, about 215 kcal/mol for protonation at the carbon atom. A discussion concerning reaction schemes for the possible interstellar production of this radical through ion-molecule processes is also provided.

LASER SPECTROSCOPY OF RARE EARTH CONTAINING DIATOMIC MOLECULES: RECENT RESULTS

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Our extensive investigation into the Spectroscopy and structure of rare earth oxides has been extended to cover dipole moment measurements and Spectroscopy of the fluorides. Stark effect experiments at sub-Doppler resolution have enabled us to determine the dipole moment of Samarium monoxide. In addition, we have obtained high resolution laser excitation spectra of HoF, DyF and YbF, both Doppler limited and sub-Doppler, which have enabled us to determine the properties of the ground and several excited states of each molecule and determine the ground state superconfigurations. Details of the analysis will be presented and discussed in terms of the predictions of ligand field theory.

HOMO- AND HETEROLYTIC BOND ENERGIES
PART 1: HOMOLYTIC BOND DISSOCIATION ENERGIES IN COMMON UNSATURATED ORGANIC COMPOUNDS

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It is shown that the homolytic bond dissociation energies (BDEs), DH°(X-R), of the X-C bond in allylic, propargylic, benzylic, cyanated and unsaturated compounds can be estimated by the simple equation:

$$DH^\circ(X\text{-}R)_{est} = DH^\circ(X\text{-}C(CH_3)_mH_{3-m}) + E_s + \Delta V_{nb} \qquad (1)$$

Where X is a wide variety of univalent atoms or substituents; R is an allylic, propargylic, benzylic, or a cyanated or unsaturated group; $DH^\circ(X\text{-}C(CH_3)_mH_{3-m})$ is the X-C BDEs in the model saturated compounds and known from our previous work; m is the degree of methyl substitution of the group R; E_s is the p-π resonance stabilization energy (RSE) of the given conjugated radical R and is independent of the nature of X; ΔV_{nb} is the steric compression relief and/or the net change of the steric interaction energies between non-bonding atoms in the compounds RX, and in the radicals R and X resulting from the C-X bond cleavage and can be estimated by Benson's method or by the MM2 program of molecular mechanism. Eq. (1) is also good for more unsaturated species and a similar approach can be extended to predict heterolytic BDEs.

Millimeter-wave Spectroscopy of HCCN and DCCN

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Free HCCN has received considerable experimental[1] and theoretical[2] attention. Interest in this molecule stems from a disagreement between *ab initio* calculations which predict a bent ground state geometry and ESR and previous microwave results[1] which conclude that a linear ground state geometry is the most plausible structure. We report here previously unobserved $K\ (l) \neq 0$ satellite transitions in the millimeter-wave region in both HCCN and DCCN. Our measurements are discussed in the context of the expected rotational spectrum for a normal linear molecule and a bent molecule and the recent IR measurements of Morter *et al.*[3]

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HIGH RESOLUTION STUDIES OF NITRIC OXIDE: RYDBERG–VALENCE INTERACTIONS AND PREDISSOCIATION DYNAMICS

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(2+1′) multiphoton excitation of $^{14}N^{16}O$, resonantly enhanced through the $(3s\sigma)A\ ^2\Sigma^+(\upsilon=1)$ Rydberg state, has been used to determine the term energies and natural linewidths of both the *e* and *f* symmetry components of individual rovibronic levels of the $(4p\pi)K\ ^2\Pi(\upsilon=2)$ Rydberg state which lie in the region of 69 000 cm^{-1}. These experiments have been conducted within a static cell utilizing two high resolution, single mode cw dye lasers in conjunction with laser induced fluorescence dip detection. Doppler-free resolution has been achieved by means of velocity selection. The term energies and natural linewidths of several rotational levels of the $(3d\delta)F\ ^2\Delta(\upsilon=3)$ Rydberg state have also been determined. The nominally forbidden $\Delta\Lambda=2$, $F \leftarrow A(3,1)$ transitions are observable because of a weak $K(\upsilon=2) \sim F(\upsilon=3)$ perturbation.[1]

(1+1′) multiphoton ionization has also been used to obtain a rotationally resolved spectrum of the $F \leftarrow X(3,0)$ band of $^{14}N^{16}O$. These experiments were also conducted within a static cell; tunable VUV radiation was obtained by frequency tripling the output of an high resolution, single longitudinal mode pulsed dye laser in Xenon gas.

A plot of the $K(\upsilon=2)$ reduced term energies shows a rapid transition from Hund's case (*a*) to case (*b*) to case (*d*) coupling resulting from S-uncoupling and L-uncoupling. This data reveals evidence for the existence of a perturbation at low N, as well as for the $K(\upsilon=2) \sim F(\upsilon=3)$ perturbation near N=11 and 12. The $K(\upsilon=2)$ natural linewidths, which correspond to lifetimes of the order of hundreds of picoseconds, are thought to be limited by predissociation.[2] These linewidths manifest a complex dependence upon N, the total angular momentum exclusive of spin, providing dramatic confirmation of both Rydberg-Rydberg and Rydberg-valence interactions.[3]

The mechanism of the $K(\upsilon=2) \sim F(\upsilon=3)$ two-state perturbation, and the pathways for predissociative decay of the $K(\upsilon=2)$ rovibronic levels will be discussed.

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Influence of Surfactant Nature on the Decay Kinetics of the Radicals from Dihydroquinolines in Micellar Solution.

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Decay kinetics of the radicals from 2,2,4,6-tetramethyl-1,2-dihydroquinoline (TMQ) and 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (EMQ) in micellar solutions of cationic (cetyltrimethylammonium bromide, CTAB) and anionic (sodium dodecylsulphate, SDS) surfactants were studied by means of flash-photolysis. It has been found, that the composition of radicals generated by photolysis depends both on dihydroquinoline and surfactant nature. In SDS solutions the spectra of short-lived radical products of the photolysis show that only cation-radicals are formed from TMQ and the mixture of cation-radicals and neutral radicals from EMQ. This is in concordance with previously estimated values of pK_a for these radicals: 10.4 and 9.4 for radicals from TMQ and EMQ respectively.

This leads to different kinetic laws for the radical decay: the first order for TMQ radicals and the second order for EMQ. The second order is connected with bimolecular reaction of two neutral radicals and neutral radical with cation-radical. In the case of TMQ no interaction of cation-radicals occurs because of Coulomb repulsion. The rate-determining stage of the reaction is therefore the formation of the neutral radicals in the reaction of cation-radical with water and TMQ, that is followed by fast bimolecular reaction of cation-radical with radical. The first order rate constant is linear with the concentration of TMQ in micellar phase $[TMQ]_M$ and is equal to $k_{eff} = (k_{H2O} + 198[TMQ]_M)$, s^{-1}, where $k_{H2O} = 22.5\ s^{-1}$, is a rate constant of the reaction of TMQ cation-radical with H_2O.

In CTAB solution only neutral radicals are formed in micellar phase and theirs decay kinetic curves consist of two parts: rapid ($50 \div 100$ ms) and slow ($5 \div 10$ s) ones. There is the second order kinetics throughout both parts. The values of the effective constants for rapid component are close to appropriate constants in homogeneous solution and comprise $\approx 2 \cdot 10^7$ and $6 \cdot 10^7$ l/(mol·s) for TMQ and EMQ respectively. The constants for slow reaction are $3 \div 4$ order lower. The rapid component is connected with the recombination of two radicals in one micelle and the slow one - in the micellar phase as a whole.

There are small amounts of cation-radicals in water phase of CTAB solution. These radicals disappear by the first order reaction with the rate constant equal to k_{H2O} in SDS solution.

KINETIC AND MECHANISTIC STUDY OF THE REACTION BETWEEN NO_2 AND CH_3SH

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The kinetics of the thermal reaction of NO_2 with CH_3SH has been studied in the static systems with different surface/volume ratios by UV spectroscopy and IR diode laser spectroscopy at six temperatures between 297 and 365 K, and in the pressures range of 20-500 mbar. The NO_2 decay profiles, in the large excess of CH_3SH, were fitted to a double exponential with a standard non-linear procedure. The values of the rate constants derived should be considered as an upper limit to the homogenous gas-phase reactions.

The first mechanistic study of the title reaction was performed by Balla and Heicklen [1] using mass spectrometry. In the present studies we employed ESR technique to identify intermediate radicals in trapped-frozen reaction samples as well as IR and GC/MS methods for analysis of the end products. The nature of the reaction products depends on the reaction conditions.

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KINETIC CHARACTERISTICS OF RADICAL REACTIONS OF NATURAL POLYPHENOLS

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The reactive potential of natural polyphenols (such as derivatives of 4-hydroxybenzoic and 4-hydroxycinnamic acids) has been studied in interaction with peroxyl radicals as well as deceleration effect in oxidation of pork fat (T= 100°C) .

It was demonstrated that derivatives of 4-hydroxycinnamic acid with COOH group separated with vinyl group from benzene ring ensure extended deceleration periods thus making more efficient oxidation inhibitors if compared to similar derivatives of 4-hydroxybenzoic acid. Methoxy group when introduced into the structure also raises inhibitor efficiency. The dihydroxyderivatives containing 2 functional hydroxy groups (such as 3,4-dihydroxybenzoic and 3,4-dihydroxycinnamic acids) are the strongest inhibitors in the series. Most of the inhibitors in these series are more efficient than conventional antioxidants (such as α-tocopherol and ionol) at high temperature oxidation of fat.

The antiradical activity of inhibitors was measured by chemiluminescence method in terms of their interaction rate with radicals. The correlation was established between antiradical and antioxidative activities depending on the amount of methoxy and hydroxy groups in the structure. The mechanism was found for the activity of dihydroxyderivatives. Quinone is the end product which produces simiquinone radical in disproportionation reaction with the initial inhibitor. The semiquinone radical is a good inhibitor for oxidation chain and does not participate in the chain propagation. This specific inhibiting mechanism provides for high efficiency of biological activity of natural polyphenols.

EXPERIMENTAL AND THEORETICAL STUDIES OF THE ELECTRONIC SPECTRUM OF Nb_2 IN THE 400-900 NM REGION

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The gas-phase, rotationally resolved, electronic spectrum of the niobium dimer molecule is reported for the first time. The molecules were produced by laser vaporisation of a niobium target rod and cooled in a helium supersonic expansion. The molecular beam containing niobium dimer molecules was interrogated in the range 400-900 nm using a pulsed dye laser to excite fluorescence. Numerous vibronic transitions with $\Omega = 0 \leftarrow \Omega = 0$ and $\Omega = 1 \leftarrow \Omega = 1$ symmetry were discovered in the region 650-690 nm. These were subsequently investigated at 200 MHz resolution using the cw output of a single mode ring dye laser. The principal features were classified into four $\Omega = 0 \leftarrow \Omega = 0$ systems originating from a common lower state of 0_g^+ symmetry, and three $\Omega = 1 \leftarrow \Omega = 1$ systems originating from a common lower state of 1_g symmetry. The two lower states are assigned as the $\Omega = 0$ and $\Omega = 1$ components of the $X^3\Sigma_g^-$ ground state, which arises from the electronic configuration $5s\sigma_g^2\ 4d\sigma_g^2\ 4d\pi_u^4\ 4d\delta_g^2$. The two spin-orbit components are split by several hundred cm^{-1} on account of a strong second order isoconfigurational spin-orbit interaction with the nearby $^1\Sigma_g^+$ state. Evidence for significant 4d orbital participation in the bonding is furnished by the short bondlegth ($r_e = 2.07781$ Å) and large vibrational frequency ($\omega_e = 424.891\ cm^{-1}$) determined for the $X^3\Sigma_g^-(0_g^+)$ state. Calculations on electronic states of niobium dimer in the 0-2.1 eV range have been performed using the Density Functional approach. Results of these calculations are found to be in good agreement with experiment for the ground state. The excited state calculations are used in an attempt to correlate the experimentally-observed electronic transitions with specific valence electronic promotions.

THEORETICAL CALCULATION OF THE ROVIBRATIONAL ENERGY LEVELS OF ATOM - DIATOM COMPLEXES BY USING DISCRETE VARIABLE REPRESENTATIONS

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We have been developing a computer program for calculating rovibrational levels of atom - diatom complexes. The computer program is based on some recent developments in the theory of discrete variable representations (V. Szalay, J. Chem. Phys. in press). We shall describe some details of our method and wish to present preliminary results obtained with our program.

THE TRANSITION DIPOLE MOMENT OF THE ν_3 BAND OF CH_3

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The methyl radical is one of the most important intermediates in chemical reactions. It is thougth to be one of the most abundant free radicals in the dark clouds of the interstellar medium. In hydrocarbon combustion, CH_3 recombination may be essential in the formation of two-carbon species and it has been considered to be the key active species in deposition of various kinds of carbon thin films from a discharge plasma.

Being its oscillator strength relatively large[1], the diode-laser infrared spectrum of the ν_2 out of plane bending vibration band at 606 cm^{-1} has been frequently used for testing the CH_3 role in several photolysis, combustion and discharge proccesses. This is not the case for the ν_3 band. Its spectral region overlaps with that of the C-H stretching bands, which could be very useful for the characterization of all the hydrocarbons involved in these processes. Besides it would be neccesary to detect interstellar CH_3 radicals, making use of the 3 μm atmospherical window. Nevertheless its dipole moment is remarkably weaker than that of the ν_2 band. Till now Zeeman modulated spectroscopy has been needed to obtain its gas phase high resolution spectrum[2] and the only datum reported about its dipole moment is that of the Ne matrix experiment in 1970[3].

In this work a new discharge-laser amplitude double modulation spectroscopic method with a difference frequency laser spectrometer[4] has been used. It allows to obtain the transmitance spectra of this band. It seems useful to characterize the above mentioned physical systems. Besides, temporal dependence of CH_3 signal with the modulated discharge has been studied. When combined with the reported values of the CH_3 recombination rate constant, it gives an estimate for the concentration of CH_3 radical in the discharge. From these data the transition dipole moment of the ν_3 band has been deduced.

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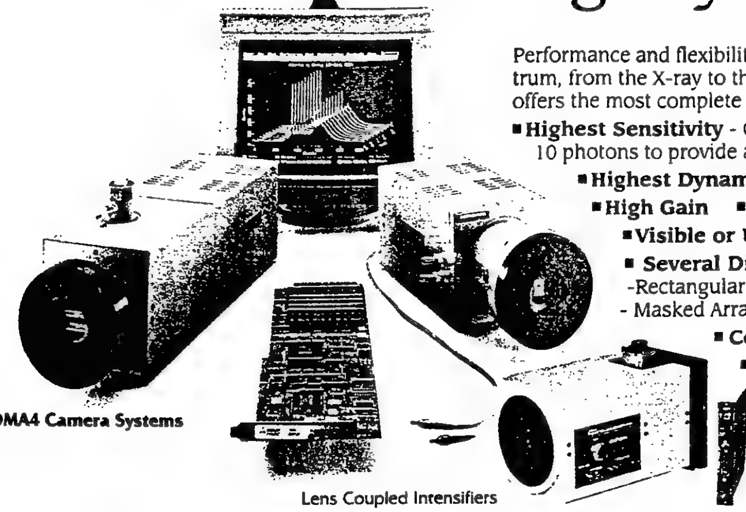

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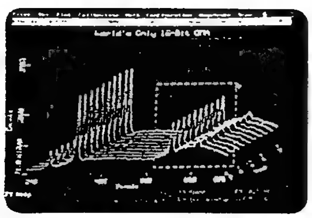

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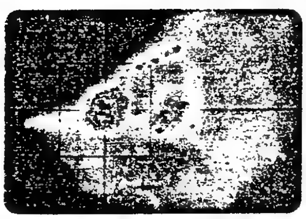

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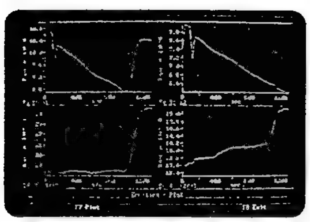

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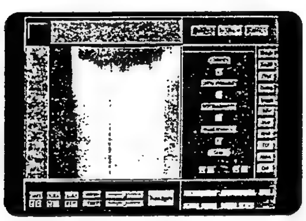

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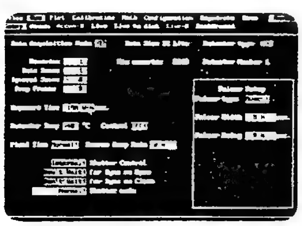

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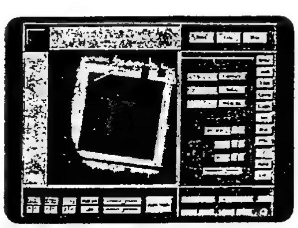

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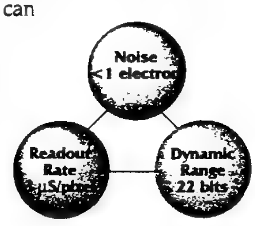

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The formation of $O_2(b^1\Sigma_g^+)$ in collisions of NH/ND($a^1\Delta$) with O_2.

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The formation of metastable $O_2(b^1\Sigma_g^+)$ in collisions of metastable NH($a^1\Delta$) with O_2 has been observed for the first time by Freitag et al. in our laboratory.[1] In those experiments, the NH(a) radicals were generated in the photolysis of HN_3 and were detected by their phosphorescence to the NH($X^3\Sigma^-$) ground state at about 790 nm. Similarly, the O_2(b) products were monitored by their forbidden transition to $O_2(X^3\Sigma_g^-)$ at ~760 nm. At that time the vibrational distribution of photolytically generated NH(a,v) was not reliably known[2] and their participation in the endothermic energy transfer process was poorly defined. In the meantime the vibrational distribution and some relaxation properties have be extensively studied.[2]

In this work we have determined the energy transfer rate constants for different vibrational energy levels NH(a,v) and ND(a,v) from a combination of lifetime and phosphorescence intensity measurements. A phosphorescence spectrum of both species is shown in Fig. 1. It clearly demonstrates the endothermic process. The source for NH/ND(a,v) was the excimer laser photolysis of HN_3, DN_3, HNCO, or DNCO. The variation of the photolysis wavelength and/or the parent molecule allowed us to study the efficiency of the different vibrational levels. The addition of N_2 made further possible to modify the vibrational distribution by relaxation.[2]. By deuteration, the vibrational energy was changed. While, for NH(a), a significant increase of the rate constant was observed with increasing vibrational quantum, the constant for the energy transfer from ND(a) does not appear to depend on the different vibrational levels studied. The absolute value for the efficiency of the energy transfer process depends on the calculated transition probability[3] for NH(a→X) which has not yet been confirmed experimentally.

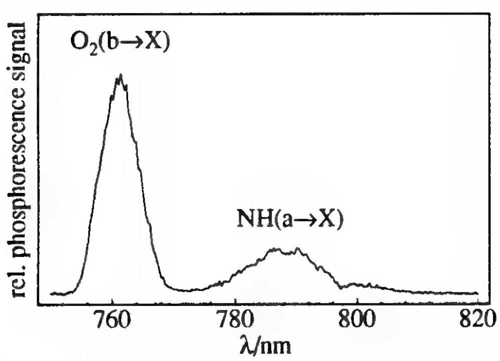

Fig. 1 Phosphorescence emission from the photolysis of HN_3/O_2 mixtures

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This work has been supported by the Deutsche Forschungsgemeinschaft (Stu59/19-2)

Spectroscopy of vibrationally excited states of CCH

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Vibrationally excited states of CCH radical up to 5000 cm^{-1} above the ground vibrational levels of the $\tilde{X}^2\Sigma^+$ state have been studied both in a flow cell and in a supersonic jet. Tentative vibrational assignments will be reported, which were made based upon the best–fit rotational constants. Nascent vibrational distribution of CCH radicals in the 193 nm–photolysis of acetylene obtained in a supersonic jet expansion has also been studied by laser–induced fluorescence. Highly vibrational excitations of CCH (Θ_v= 0.87) were found. The vibrational distribution of CCH is generally agreeable with previous studies by photofragment time–of–flight experiment.[1,2] The (v, J, T) correlation of the predominant CCH radicals will also be given.

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Diode Laser Jet Spectroscopy of Hexafluorobenzene in the 10 μm Region

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The absorption spectrum of hexafluorobenzene (C_6F_6) around 10 μm has been measured in a pulsed supersonic jet using diode lasers. In the jet spectra the most intense room temperature features at 1000 and 1022 cm^{-1} are rotationally resolved. They arise from two perpendicular bands one of which (1022 cm^{-1}) is predominantly the ν_{13} C-F stretching fundamental whilst the other is a combination band of the same e_{1u} symmetry in Fermi resonance with it. The upper state of the 1022 cm^{-1} band is also perturbed by a local R_z-Coriolis interaction. Two other weak bands at 1002 and 1012 cm^{-1} have also been observed. A set of effective parameters for these bands have been derived. The origins of the main bands are 999.28729(6) and 1022.28442(6) cm^{-1}.

Rotational analysis of a $^4\Gamma$-$^4\Phi$ transition in the spectrum of titanium hydride

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Gaydon and Smith[1] observed three electronic transitions in the TiH molecule between 490 and 540 nm. They used a flash absorption technique after a shock-wave in titanium powder and hydrogen. Gaydon later presented a partial analysis[2] of the system at longest wavelenths. This system has later been treated both theoretically (Anglada *et al.*[3]) and by experiments (Steimle *et al.*[4]) and both theory and partial analyses indicate that this is a $^4\Gamma$-$^4\Phi$ transition.

Using a King type furnace and a FT-spectrometer we have recorded this system in thermal emission at 2500°C and have now been able to analyze all four subbands. The four sub-bands have heads at 538.18, 537.01, 536.15, and 535.47 nm and they are degraded to shorter wavelengths. The analysis was to a certain amount chequed by LIF results using a Kr^+ laser. Perturbations are found in the upper $^4\Gamma$ state. Sofar no $\Delta\Omega=0$ intercombination bands have been identified

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THE INFRARED SPECTRA OF NO_2^+, NO_2^-, AND NO_3^- ISOLATED IN SOLID NEON

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When a mixture of NO_2 with a large excess of neon is codeposited at approximately 5 K with a beam of neon atoms that have been excited in a microwave discharge, very prominent absorptions assigned to ν_3 of NO_2^+ and of NO_2^- appear, as do weak absorptions assigned to the $(\nu_1 + \nu_3)$ combination band of each of these ionic products. The product assignments are supported by detailed isotopic substitution studies, which also make possible normal coordinate analyses for these two species. The vibrational energy levels of NO_2^+ isolated in a neon matrix are in good agreement with those recently obtained[1] in a high resolution triple-resonant ionization study of gas-phase NO_2 with zero kinetic energy photoelectron detection. When O_2 is also present in the sample, the infrared-active stretching fundamental, ν_3 (e′), of NO_3^- appears. The cation field is sufficiently weak that splitting of the degeneracy is almost completely avoided.

Footnotes and References

* Guest Researcher at the National Institute of Standards and Technology.

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SPECTROSCOPIC AND KINETICS STUDIES OF THE NO_3 RADICAL: IMPLICATIONS FOR THE ATMOSPHERE

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The physical properties of the Earth's atmosphere are profoundly influenced by a variety of theoretically interesting molecules which are produced from photochemically initiated processes. The nitrate radical, NO_3, which serves as the primary chemical intermediate between the chain carriers (NO and NO_2) in the NO_x-catalyzed destruction of ozone and the temporary NO_x reservoirs (N_2O_5 and HNO_3), is one important atmospheric constituent for which an adequate description of its physical properties has remained elusive. In order to further characterize the atmospheric role of NO_3 we have studied the rovibronic structure and the reaction chemistry of NO_3 using Fourier transform infrared spectroscopy.

NO_3 spectroscopic data have been obtained between 700 and 6000 cm^{-1} at 220 K and 298 K. The observed temperature dependences of the infrared bands are of significance in terms of the vibrational band assignments as well as with respect to the debate concerning the ground state geometry of NO_3.

We have also observed new infrared and ultraviolet spectral features arising from the reaction

$$NO_3 + OClO \rightarrow Products$$

below temperatures of 250 K. We assign these features to chloryl nitrate (O_2ClONO_2), a novel compound of potential atmospheric significance. We will present a characterization of the reaction phenomenology and discuss the possible significance of chloryl nitrate as a reservoir of inorganic chlorine in the Earth's atmosphere.

THE VIBRONIC STRUCTURES OF CH_3O AND CD_3O ($\tilde{X}\ ^2E$) AND ($\tilde{A}\ ^2A_1$)

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The CH_3O radical is a prototypical C_{3v} symmetric top molecule with one unpaired electron in an orbitally degenerate electronic ground state, $\tilde{X}\ ^2E$. Thus, CH_3O is a nice example of a molecule that is subject to a Jahn–Teller effect. In addition, it is also a unique model case for studying the unimolecular dissociation dynamics of highly vibrationally excited molecules.

In this report, we present a complete rotationally resolved investigation of the ($\tilde{X}\ ^2E - \tilde{A}\ ^2A_1$) electronic transition system of both CH_3O and CD_3O. The experimental techniques which were employed are Laser Induced Fluorescence (LIF) excitation, Dispersed Fluorescence (DF), and Stimulated Emission (SE) spectroscopy in a seeded supersonic free jet expansion.

In the LIF excitation spectra, a total of 13 different vibronic band types were distinguished unambiguously by their rotational structures. This allowed for definite assignments of the vibronic symmetries and angular momenta of the vibrational states which occur in the LIF excitation spectra. In especially, the analysis of numerous "hot bands" provided a key access to information on the degenerate modes in the $\tilde{A}$ state.

From the DF and SE spectra, the absolute term energies of the vibronic states in the $\tilde{X}$ electronic ground state could be measured. Here, different vibronic assignments had to be made for a number of levels than assumed previously. A Jahn–Teller analysis results in a quantitative picture of the linear and quadratic vibronic interactions in the $\tilde{X}$ electronic ground state.

The impact of these results will be outlined pertaining to our understanding of the intramolecular vibrational dynamics and the unimolecular dissociation reaction of highly excited CH_3O ($\tilde{X}$) to $H + H_2CO$.

HIGH RESOLUTION INFRARED EMISSION SPECTROSCOPY OF THE TRANSIENT MOLECULE HNSI

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Iminosilicon HNSi is a possible reaction product in the nitrogen-silicon chemistry of interstellar clouds (1). Only the 00^00 and 10^00 levels of HNSi in its linear fundamental electronic state have been observed recently at high resolution (2-3).

We report here the observation by emission Fourier transform spectroscopy with 0.005 cm^{-1} resolution of four new bands of HNSi, produced in a rf discharge of a silane and nitrogen mixture. These bands, centered at 3450.461, 3584.804, 3446.385 and 3569.082 cm^{-1}, have been respectively assigned to the $2v_1$-v_1, v_1+v_3-v_3, $2v_1+v_3$-(v_1+v_3), and v_1+v_2-v_2 transitions.

In addition to the spectroscopic parameters of seven new levels, we determined for the first time the rotational and vibrational equilibrium parameters of HNSi. They confirm the theoretical results of Botschwina and coworkers (4), which are in very close agreement with our experimental observations.

This work was supported by the CNRS "Groupe de Recherche sur la Physico-Chimie des Molécules et des Grains Interstellaires"

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J. Chem. Phys. 95, 7769 (1991)

Realisation of a discharge in a supersonic expansion for concentration modulation of Van der Waals clusters and for radical production

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We have investigated several setups for a discharge in a supersonic jet expansion. One possible application of this experimental setup should be the observation of radicals at very low rotational temperatures, which will be especially helpful in order to simplify complicated spectra. A realisation of a corona excited supersonic expansion in a nozzle was reported by Engelking *et al*[1]. Comer and Foster [2] recently reported a corona excited supersonic slit jet. This device was used to measure the infrared spectrum of CS and NH_2.

We have built up a design, that allows to maintain a discharge over the whole length of the slit nozzle (3cm). Initially, we have used this discharge for concentration modulation of Van der Waals clusters. The discharge was switched on and off with a repetition rate of 3 kHz, which causes a decrease in the density of the Van der Waals clusters. Using this concentration modulation we could improve the sensitivity of our spectrometer - a computer controlled diode laser in combination with a cw 2-dim jet) considerably and we were able to measure the transition from the ground state to the combination band of v_{CO}=1 and the first excited bend of Ar-CO, which has not been reported so far.

As a first result of the application towards the generation of radicals we can report the observation of transitions in the R-branch in the groundstate of NO^+, generated in a discharge of He and NO.

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THE DISSOCIATIVE CHARGE EXCHANGE SPECTRUM OF MOLECULAR NITROGEN

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[2]SRI-International, Menlo Park, U.S.A.

The N_2 molecule is one of the most throughly studied,[1] but also one of the most perturbed[2] and complicated spectra among diatomic molecules. In the energy region between 12 and 15 eV above the v=0 N_2 ground state the spectrum is characterized by n=3 Rydberg series converging to the X $^2\Sigma_g^+$ and A $^2\Pi_u$ N_2^+ states.

We have studied these states with translational spectroscopy.[3] A beam of N_2^+ ions (containing both X and A state) are neutralized by a charge transfer reaction on Cs vapour in a cell. In a one electron process, N_2^+ X state ions form Rydberg states on the X core and A state ions on the A core. The Rydberg states couple with repulsive valence states and dissociate into their atomic fragments. Our observable is the kinetic energy released during dissociation, which is obtained by measuring the mutual distance of the fragments and their time difference with a two particle position- and time sensitive detector. The kinetic energy release spectra reveal the spectroscopy and dynamics of the Rydberg states.

The X $^2\Sigma_g^+$ and A $^2\Pi_u$ N_2^+ states have an allowed dipole transition. By transferring population from the (v=0) X $^2\Sigma_g^+$ to the (v'=1 or 2) A $^2\Pi_u$ using a Ti:Al_2O_3 laser coaxial to the N_2^+ beam, the v' peaks of the Rydberg states on the the A-core increase in intensity, while the v=0 peaks of Rydberg states on the X-core decrease in intensity. This makes it possible to assign the vibrational number of the peaks.

Up till now it was thought that the v=0 of the (3sσ) F $^3\Pi_u$ state lied at 12.97 eV,[1] however one of the results of the experiments is that it lies in fact at 12.75 eV.

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THE REACTIVITY AND SPECTRAL PROPERTIES OF NITROXYL AND PHENOXYL RADICALS RESULTING FROM THE HYDROQUINOLINES OXIDATION

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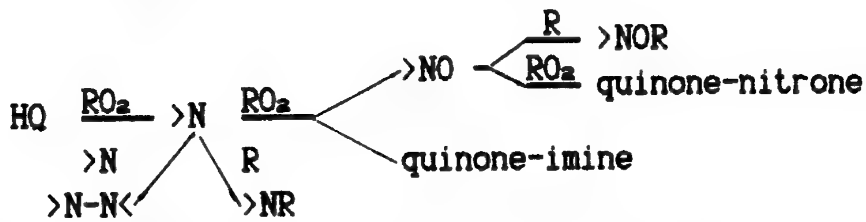
The oxidation of hydroquinolines (HQ) with peroxyl radicals (RO_2) and oxygen occurs via the formation of free radicals whose nature and properties depend on the substituents in the aromatic ring of HQ. In the case of di- and tetrahydroquinolines containing alkyl or alkoxysubstituents short-living aminyl (>N) and sufficiently persistent nitroxyl (>NO) radicals are formed:



The nitroxyls derived from 2-spyro-4-(spyro-tetrahydrofuryl-2')-1,2,3,4-tetrahydroquinoline (I) and 6-triphenylmethyl-1,2,4-trimethyl-1,2-dihydroquinboline (II) are remarkable stable and can be isolated in crystalline form. I is a convenient free radical scavenger because in the reaction with RO_2 it yields corresponding quinone-nitrone (λ_{max} = 371 nm, ε = 1,8 10^4 l/mol cm). The reaction of I with alkyl radicals (R) gives ether >NOR that has no absorbtion band in the visible region of spectrum.

HQ hydroxysubstituted in position 6 or 8 interact with RO_2 at OH-groups and form phenoxyl radicals as primary oxidation products. We have shown that PhO(1) resulting from 6-OH-HQ disproportionates as H-donor with any free radicals (R, RO_2, Pho, >NO) to form corresponding quinone-imine. PhO(2) derived from 8-OH-HQ is sufficiently persistent and reacts with RO_2 to form 5,8-p-quinone. The rate constants of the reactions of nitroxyl and phenoxyl radicals with a number of free radicals have been determined.

Photodissociation of CH_2.

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Photodissociation of CH_2 is of considerable astrophysical interest. Through its first three excited triplet states ($1\ ^3A'$, $2\ ^3A''$, and $3\ ^3A''$) CH_2 can photodissociate into CH + H. Studying the photodissociation through the $2\ ^3A''$ state is especially challenging to the chemical dynamicist because dissociation into C + H_2 can occur as well.

Recently, full 3-D *ab initio* (MRD-CI) potential energy surfaces (PES's) have been calculated by Beärda et al.[1] for the excited states and the ground ($1\ ^3A''$) state, as well as the transition dipole moment functions connecting these states. The *ab initio* data have been used to perform wave packet calculations on photodissociation through the first excited ($1\ ^3A'$) triplet state [2,3]. Also, the emission spectrum of photodissociating CH_2 has been computed for excitation frequencies corresponding to known laser lines. The calculations predict spectra containing strong progressions in the symmetric stretch vibration, but also fairly strong progressions in the bending mode. Measurements of these spectra should yield the frequencies of the symmetric stretch fundamental and its overtones, which are unknown at present, and present the first empirical evidence concerning the existence of the first excited $1\ ^3A'$ state.

Calculations on photodissociation through the second excited ($2\ ^3A''$) triplet state are now in progress. To enable a good description of the dissociation into $C(^3P)$ and H_2, a 3-D treatment is necessary. We hope to present results of these calculations (including the branching ratio for dissociation into CH+H and C + H_2) at the meeting.

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Vibrational Effects in Reactions of Small Molecules

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The recently developed STIRAP technique (stimulated Raman scattering involving adiabatic passage) allows complete population transfer in molecules such as Na_2 as well as atoms, e.g. Ne^* using **single mode cw radiation.**

The extension of STIRAP to molecules whose transitions require UV radiation leads to the need of **pulsed lasers** in order to reach the adequate power. The relatively poor coherence properties of such lasers require a consideration of the effect of phase– and amplitude fluctuations. We will present the conditions for a successful implementation of pulsed STIRAP derived from analytical and numerical studies. Experimental results for vibrational excitation of the NO–molecule will be presented.

Implementation of the STIRAP technique with cw lasers for routine scattering experiments has now been demonstrated. We have studied the chemoluminescent channel of the reaction $Na_2(v) + Cl \longrightarrow NaCl + Na^*$ for many vibrational levels up to $v = 27$. The cross section is strikingly linear with the vibrational energy $E(v)$. Experimental efforts are under way to compare the effect of vibrational and collisional energy on the reaction. We will compare the experimental data with numerical results from phase space calculations as well as from a harpoon model.

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ELECTRONIC SPECTROSCOPY AND FLUORESCENCE LIFETIMES OF EXCITED STATES OF BISMUTH MONOIODIDE

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In the context of an extensive research of the electronic spectroscopy and dynamics of excited states of bismuth monohalides, a careful study of the BiI molecule is being performed by laser induced fluorescence.

The fluorescence of BiI molecule was excited by a dye laser pumped by a Nd-YAG laser, delivering pulses (of 6 ns long and a narrow linewidth of 0.08 cm^{-1}) from 2-6 mJ in the spectral interval 416-475 nm to get excitation spectra of the A'-X and B-X systems in this molecule.

BiI was prepared by heating the BiI_3 and bismuth metalic inside an evacuated stainless steel cell in an oven at 500 °C. Undispersed fluorescence of the A'-X system in the 432-475 nm wavelength excitation range and B-X system in the 416-430 nm wavelength excitation range was excited. Excitation spectra for both systems were obtained by first time and the most intense vibrational transitions were assigned.

Fluorescence lifetimes measured by first time for emission of different vibrational levels of the B state were in the range 0.25-0.5 μs at 500°C, and 0.65 μs for the A' state at the same temperature. No significative variations were found for different rotational transitions.

Fragment Angular Distributions from Photolysis of Oriented Molecules

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The complete experimental specification of the initial and final states in a reactive process has long been the goal of experimental chemical dynamics. For the simplest unimolecular reaction, photodissociation, progress has been made to very near this goal. We here report preliminary results from the first state-selective study of a direct photolysis. The angular distribution of fragments produced from the photolysis of oriented methyl iodide molecules, prepared in selected $|JKM\rangle$ states by hexapole focusing, is state-selectively detected by two-dimensional ion imaging. For the simple, direct, photolysis of CH_3I at 266 nm, the angular distribution reflects the shape of the prepared symmetric top wave function. With detection of the kinetic energy and angular distribution of single fragment states by polarized radiation, a photolysis can be probed in essentially complete detail.

We describe the (classical) general angular distribution of photofragments from the dissociation of an oriented molecule, with the aim of determining how dynamical processes are reflected in such a distribution. Different dynamical situations which produce identical angular distributions in a standard photodissociation experiment can in principle be distinguished in the dissociation of initially oriented molecules. We provide specific theoretical illustrations of the increased persistence of information about the shape of the molecule-fixed (dynamical) recoil distribution in the photolysis of initially oriented molecules.

COHERENT CAVITY RING DOWN SPECTROSCOPY

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Cavity ring down spectroscopy (CRDS) was introduced as a sensitive gas phase direct absorption technique by O'Keefe and Deacon [1] in 1988. The method is based upon the measurement of the rate of absorption rather than the magnitude of absorption of a light pulse confined within a closed optical cavity. By measuring the cavity decay time the problems associated with pulse-to-pulse fluctuations of the laser system are circumvented.

Application of direct absorption techniques in high pressure samples, e.g. flames and plasmas, is advantageous since Beer's law can be used to extract quantitative *absolute* concentration data which is nearly impossible by other techniques.

In this contribution we report the use of *coherent* cavity ring down spectroscopy (COCRDS), a form of CRDS that uses a long coherence length laser and a short resonant cavity. The multi-mode structure of the cavity has been explicitly manipulated to allow a high spectral resolution. The improved spectral resolution also means a gain in absolute detection sensitivity. In addition, we here report the first extension of CRDS to the UV. COCRDS is performed around 300 nm on OH in a flame as well as around 206 nm on the weak Cameron band of CO in a low pressure cell.

In particular we have obtained absorption spectra of rotationally (up to N"=27) and vibrationally (v"=1 and 2) excited OH in a CH_4/air flame near 298 nm via COCRDS. A test of the Maxwell Boltzmann law was thereby performed and the quantitative nature of COCRDS was demonstrated. Detection of the band orgin of the 0-0 vibronic band of OH was so easy that we even could observe a strong signal from almost thermalized OH ($T_{rot} \approx 400$ K) some 10 cm above the top of the visible part of the flame, establishing a detection limit for room temperature OH using COCRDS of 10^{11} radicals/cm^3. Rotational line intensities and the absolute transition strength of the spin forbidden Cameron band in CO have been determined using this absorption technique.

COCRDS can be used from the IR into the UV and with a cavity ring down time comparable to typical radiative lifetimes of excited molecules the technique can be applied in multiple resonance experiments as well. Specifically, coherent cavity ring *up* as a sensitive way of detecting stimulated emission transitions should be feasible.

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PHOTOPOLYMERIZATION OF METHYL-METHACRYLATE IN PRESENCE OF SOME PHTHALOCYANINE PIGMENTS

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ABSTRACT

The ability of copper phthalocyanine, copper biphthalocyanine and its metal free to initiate the photopolymerization of methyl methacrylate was studied in comparison with copper(II)chloride. The effect of these pigments on the conversion, rate of polymerization and molecular weights was determined and calculated.

It was found that the various concentrations of the studied pigments deactivate the photoaqueous polymerization of methylmethacrylate, and increasing the concentration has a retarding effect.

These results revealed that the photopolymerization reaction is a free radical mechanism which is to be discussed in detail in the text. The role of the phthalocyanine and biphthalocyanine pigments in retarding the photopolymerization process is expected to be due to a screening and quenching effect.

Determination of Herman-Wallis factor of CF radical by high resolution FTIR spectroscopy

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The infrared spectrum of CF radical has been measured by using high resolution FTIR spectrometer at the resolution of $0.004 cm^{-1}$. The CF was generated by the electric discharge of the mixture of Ar and CF_4 (100:1). The reliable molecular constants for V=1 state have been obtained using a similar Hamiltonian used by Kawaguchi et al.[1]

From the analysis of the intensity distribution of observed vibration-rotation lines with Herman-Wallis theory[2], the ratio of permanent (μ_0) and transition dipole moment (μ_1) has been determined to be (μ_0/μ_1)=-4.6. The value of μ_0 determined by Saito et al.[3] gives μ_1=0.14(7)D. The direction of transition dipole is found to be opposite to that of permanent diople, which agrees with the ab initio MO calculation (MP2/6311G*).

This work was supported by New Energy Industrial Technology Developement Organization (NEDO).

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VARIOUS FREE RADICALS AS CHAIN CARRIERS IN THE OXIDATION OF CYCLOHEXANE CARBOXYLIC ACID

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The oxidation of cyclohexane carboxylic acid (CHA) has been studied in detail both as a prototype for degenerate chain branching process and a possible source for the production of cyclohexanone. The kinetics of product accumulation (by GCMS); the effect of inhibitors, initiators and catalysts as well as chemiluminescence phenomena have been followed quantitatively.

It has been established that the process at the early stages of the conversion is an oxidative decarboxylation with two chain carriers: tertiary and secondary carboxyl peroxy radicals, formed by the attack on α and β hydrogen atoms in the cyclo-ring, while direct attack on the carboxylic hydrogen is negligible in autoxidation.

Kinetic calculations revealed that CO_2 formation proceeds in two parallel pathways: (i) simultaneously with the formation of cyclohexanone and (ii) omitting the formation of the latter by the oxidation of hydroxy- and keto-carboxylic acid. The rate constants of the chain propagations have been calculated.

Based on experimental data and calculations, a "heuristic" mechanism is suggested in order to describe the process.

The *Possible Mechanism* of the process has been compiled by a computer program and reduced using complexity factors and thermochemical kinetic analysis of the elementary reactions included in the possible mechanism.

The corresponding treatment of the reduced mechanism resulted in the sequence *Network* of the overall reaction representing the different pathways leading to primary products observed experimentally.

FAR INFRARED LASER MAGNETIC RESONANCE OF HOCO AND DOCO

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Far infrared laser magnetic resonance spectroscopy has been used to measure components of many rotational transitions in *trans*-HOCO and its deuterated isotopomer in the ground $\tilde{X}\ ^2A'$ electronic state. The assigned transitions are all *b*-dipole in character, obeying a rotational selection rule of $\Delta K_a = \pm 1$. These new data therefore complement the previously detected millimeter wave and infrared spectra [*J. Chem. Phys.* 97 3989, 3996 (1992)] which consisted of just *a*-dipole transitions. The new data are used to refine the coefficients of the K_a dependant terms in the effective Hamiltonian for the molecule. For HOCO, small hyperfine splittings were resolved in several resonances. Their analysis points to a very small Fermi Contact interaction, the hyperfine splittings are apparently dominated by the spin-spin dipolar interaction.

These data provide new avenues for future studies of the kinetics of chemical reactions involving this important, and heretofore elusive, radical. They also allow a refinement of the structural parameters, however spectroscopic information for the ^{13}C substituted species is desirable from this point of view.

Work at Brookhaven National Laboratory was performed under Contract No. DE-AC02-76CH00016 with the US Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

THEORETICAL INVESTIGATION OF VIBRATIONAL SPECTRA OF PROTONS SOLVATED IN ARGON MATRIX

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In 1972 Bondybey and Pimentel[1] reported the appearance of an absorption band at 905 cm^{-1} in the IR-spectrum of Ar/H_2 matrix samples which were codeposited after the gas mixture passed through a glow discharge. This absorption was assigned to vibrations of interstitial neutral H-atoms trapped in octahedral sites in the argon lattice. However, in the set of subsequent experiments[2-4] the 905 cm^{-1} band was reassigned to the Ar_nH^+ charged species. In order to explain the origin of this band, the Ar_nH^+ ionic clusters were studied in their electronic ground state by the nonempirical methods[5-7].

In present report the results of ab initio calculations of geometric structure, stability and vibrational srectra for Ar_nH^+ ($n = 1-4$) are submitted. Four different types of atomic basis sets (6-31G**, double-zeta(DZ), DZ+d_{Ar}, DZ+d_{Ar} +p_H) were employed. Based on these results, the $Ar_{n-2}(Ar_2H^+)$ structure (with (n-2) argon atoms attracted to the linear Ar_2H^+ core ion by polarization forces) is suggested. The centrosymmetric ($D_{\infty h}$- symmetry) structure for Ar_2H^+ is obtained at our DZ, DZ+ polarization calculations in agreement with a fairly high level of theory used in papers[6,7]. Nevertheless, none of the calculated in[5-7] vibrational spectra for $Ar_2H^+(D_{\infty h})$ has sufficient bases to be attributed to an absorption observed at 905 cm^{-1}. This absorption band origin is discussed on the basis of calculations of the Ar_3H^+ and Ar_4H^+ vibrational spectra.

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Diode Laser Spectroscopy of the Propargyl and Cyanomethyl Radicals

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The ν_6 (C≡C-H, out-of-plane bend) fundamental band of the propargyl radical ($CH_2C≡CH$) was observed by time resolved infrared diode laser spectroscopy. The propargyl radical was produced by the photolysis of allene (C_3H_4) or propargyl chloride ($ClCH_2C≡CH$) with 193 nm, ArF excimer laser light.

So far more than 30 signals were assigned to $^rQ_0$ and $^rR_0$ branch transitions, and several lines tentatively to $^pP_2$ branch transitions. Most of the $^rR_0$ and $^pP_2$ branch transitions were observed as doublets due to the spin-rotation interaction in the $^2B_1$ ground electronic state. The effective molecular constants derived from the $^rQ_0$ and $^rR_0$ branch transitions are $(B+C)/2$ = 0.31182(24) and 0.31166(22) cm^{-1} for the ground and ν_6 state, respectively, $(B-C)/2$ = 0.005021(70) cm^{-1} for the ν_6 state, and D_N= 1.94(80)$\times10^{-6}$ and 1.58(74)$\times10^{-6}$ cm^{-1} for the ground and ν_6 state, respectively. The subband origin for K = 1 ← 0 is 696.02353(54) cm^{-1}. The molecular constants are consistent with recent experimental results for the ν_1 band[1] and *ab initio* calculation[2]. The ν_6 band origin estimated with the above constants is 686.4 cm^{-1}, which is close to the value 687 cm^{-1} reported by a matrix isolation study[3].

Similarly, the ν_5 (CH_2 wagging) fundamental band of cyanomethyl radical (CH_2CN), which is isoelectronic with the propargyl radical, was observed by the photolysis of chloroacetonitrile ($ClCH_2CN$). So far, 15 signals for the K = 3 ← 2 branch were identified, which were observed as doublets or quartets due to the spin-rotation interaction and asymmetry splitting. The molecular constants derived are consistent with the results of MW spectroscopy[4]. The subband origin for K = 3 ← 2 is 705.8826(11) cm^{-1}.

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POSTER SESSION C

Wednesday 8 September 1993
19.30 u

ESR AND OPTICAL SPECTROSCOPIES OF NITROGEN ATOMS ISOLATED IN SOLID QUANTUM HELIUM MATRIX.

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The ultracold matrix isolation of the active particles by helium atoms has a wide prospects for spectroscopy and low temperature chemistry. At present the extensive investigations of the foreign particles captured by large liquid ^4He clusters are carried out [1,2]. In another approach realized by us, upon injection of the gas phase helium beam containing the impurity atoms and molecules into superfluid helium the impurity-helium solid phase (IHSP), comprising "sticking together" Van-der-Waals impurity helium solid clusters, has been obtained [3].

The principal advantages of the IHSP for matrix isolations of active species have been demonstrated by investigations of N atoms stabilized in such phase. The measurements of the element composition of this IHSP gave the stoichiometric ratio values $S=[He]/[N+N_2]$ equal to 12-14. The ESR investigation supported the presence of the high relative concentrations of N atoms: $[N]/[N_2] \sim 0.2$-0.5 in IHSP. The reliable isolation of the active particles by low-polarizable He atoms was proved by these results. The IHSP was found to exist up to the temperatures so high as 8K.

The characteristics of the metastable N atoms luminescence (α group, $N(^2D-^4S)$) in IHSP have been studied. The spectra and lifetimes was found to be significantly different from known so far. The extremely long - lived ($\tau \sim 3 \cdot 10^3 s$) afterglow belonged to the $N(^2D - ^4S)$ atoms transitions ($\lambda \sim 522nm$) firstly has been observed. The spectrum of the luminescence was wide enough ($\sim 30cm^{-1}$) and shifted to red ($\sim 80cm^{-1}$) from its position in vacuum.

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THE FAR–INFRARED SPECTRA OF THE TEN NEW FREE RADICALS DISCOVERED IN A YEAR

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By exploiting recent developments in far–infrared LMR spectroscopy, we have been able to detect at least ten new free radical spectra in the year September 1991 to August 1992 (when JMB was on sabbatical leave in Boulder). The species concerned are summarized below:

Species	State	Transition	Laser wavelength (μm)
^{17}O	^3P	$J = 1 \leftarrow 2$	63.14
^{28}Si, ^{29}Si	^3P	$J = 2 \leftarrow 1$	68.72, 68.09
^{27}Al	^2P	$J = \frac{3}{2} \leftarrow \frac{1}{2}$	90.2, 89.0
^{32}S	^3P	$J = 0 \leftarrow 1$	56.7, 56.5
Fe	^5D	$J = 0 \leftarrow 1, 1 \leftarrow 2$	110.7, 110.4, 54.1
$^{14}N^+$	^3P	$J = 1 \leftarrow 2$	207.8, 203.6
$^{19}F^+$	^3P	$J = 0 \leftarrow 1$	67.25, 67.2
OH^+	$a^1\Delta$	$J = 3 \leftarrow 2$	101.3, 100.8
NH^+	$X^2\Pi$	$N = 3 \leftarrow 2$, $J = 3\frac{1}{2} \leftarrow 2\frac{1}{2}$	110.7, 108.8
		$J = 2\frac{1}{2} \leftarrow 1\frac{1}{2}$	
HSiF	a^3A''	?	68.09

The spectra of the ionic species were all observed within the discharge plasma produced by the new microwave discharge source which has been described in our other poster presented at this meeting. This source is also capable of producing molecular species in vibrationally excited and metastable levels.

HOW TO DISCOVER THE SPECTRA OF TEN NEW FREE RADICALS IN ONE YEAR: DEVELOPMENTS IN FAR–INFRARED LASER MAGNETIC RESONANCE

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Two major developments for LMR Spectroscopy at far–infrared wavelengths have led to the observation of a large number of new spectra. The first is the extension of the range of routine operation of the spectrometer to shorter wavelengths (down to 40 μm). This has been achieved by reducing the internal diameter of the far–infrared pumping cell from 2.0 in (50.4 mm) to 0.75 in (19.0 mm). In this way, much better overlap between the gain medium and the far–infrared laser radiation field is achieved at shorter wavelengths. It is therefore much easier to achieve lasing action on known optically pumped FIR laser lines. Furthermore, we have discovered several new, short wavelength laser lines which had not been reported previously. As a result, there is now much better coverage of the region 100 to 40 μm (100 to 250 cm^{-1}) which increases the chance of detecting transitions in open shell species at these wavelengths (mostly fine structure transitions).

The second development is the construction of a new microwave discharge source for the observation of free radicals, including ions, within the discharge plasma. The new source is a modification of the "Evenson" cavity[1], a one quarter wavelength long coaxial cavity tuned to operate at 2450 MHz. The design has been changed so that the discharge forms at the edge of the device. Under the influence of rapid pumping, the resultant discharge plasma can be made to extend out into the far–infrared radiation field. In this way, the components of the plasma can be sampled directly. Not surprisingly, there is a strong interaction between the plasma and the applied magnetic field in an LMR experiment, possibly increasing the plasma density. We have been able to detect a variety of short–lived free radicals in the discharge, vibrationally excited molecules, metastable species and molecular ions.

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Vuv photolysis of radicals: NH_2 and CH_3

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In general, the photochemistry of radicals, in particular NH_2 and CH_3, is not well understood. Methyl, CH_3, is a key radical in hydrocarbon chemistry and its properties are therefore of great interest. Its absorption spectrum has been thoroughly studied by Herzberg[1)] and a number of Rydberg states have been assigned by him and recently by Hudgens et al[2)] using REMPI. For NH_2 some absorption features leading to different dissociation paths have been previously calculated by Saxon et al.[3)] Photolysis processes in radicals became of interest in the laboratory since its products could be monitored in the excimer laser photodissociation of their parent molecules.[4)]

In this work, radicals were produced in discharge flow systems by appropriate chemical reactions. The flowing mixtures of radicals, other products, and parent molecules were irradiated by tunable vuv light from the electron storage ring of the Berlin synchrotron (BESSY) or by lines from atomic resonance lamps. Preferably the production of electronically excited fragments such as $NH(A^3\Pi)$, $NH(c^1\Pi)$ from NH_2 and $CH(A^2\Delta)$, $CH(B^2\Sigma^-)$ from CH_3 was monitored by light from allowed transitions to lower states. Results were obtained in form of excitation spectra in the range from 200 to 105 nm and photofragment-fluorescence spectra at fixed wavelengths. As an example, an excitation spectrum for the formation of NH(A) from NH_2 is shown in Fig. 1. An assignment of the different emission regions will be attempted. Further information will be given on dynamics of the photodissociation and the photolysis process $CH_3 \rightarrow CH(A,B) + H_2$.

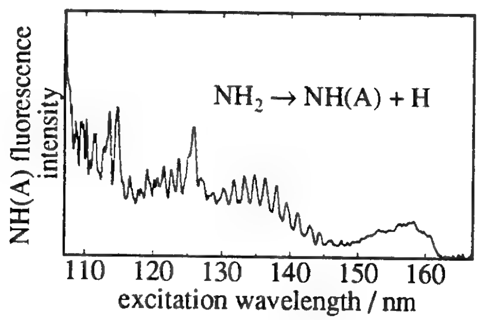

Fig. 1 NH_2 excitation spectrum

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This work has been supported by BMFT, contract No. 05432FBIO

PREDISSOCIATION IN THE $\tilde{A}\,^2A'$ STATE OF HNF (DNF): NH (ND) PHOTOFRAGMENT EXCITATION SPECTROSCOPY

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We recently reported the first observation[1] by laser fluorescence excitation of the Renner-Teller molecule HNF and its isotopomer DNF. Because of the large change in the bond angle upon electronic excitation, the observed $\tilde{A}\,^2A' - \tilde{X}\,^2A''$ band system displays a long progression in the bending quantum number v_2'. As in the flash photolysis absorption study by Woodman,[2] the K structure of the bands simplifies with increasing v_2', suggesting the importance of nonradiative decay processes for higher K' stacks. We also measured decay lifetimes for a number of HNF and DNF $\tilde{A}\,^2A'$ excited levels.[1] The decay rates, scaled approximately by the v^3 factor, were found to increase substantially as the excited state energy became greater than a threshold value. This threshold, at approximately 23,800 ± 500 cm^{-1} above the HNF($\tilde{X}\,^2A''$) zero-point level, was tentatively identified as the onset of excited-state predissociation. There are several possible spin-allowed dissociation pathways, with similar threshold energies, for this molecule: $HF(X^1\Sigma^+) + N(^2D)$, $NH(X^3\Sigma^-) + F(^2P)$, and $NF(X^3\Sigma^-) + H(^2S)$. Very recently, we reported[3] the direct detection of the ND fragment from the predissociation of DNF excited to energies near that of its $\tilde{A}\,^2A'$ (0,6,0) vibronic level in a pump-probe laser excitation experiment. NH and ND photofragment excitation spectra and fragment rotational state distributions will be presented for excitation of a variety of HNF and DNF $\tilde{A}\,^2A'$ levels. This technique has allowed the observation of higher levels for which parent molecule fluorescence cannot be detected. The implications of these results on the excited state predissociation dynamics will be discussed.

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FIR LMR Spectra of the Monobromomethyl Radical

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In spite of its potential atmospheric importance, little attention has been paid to the monobromomethyl radical. Here we report the detection of CH_2Br and CD_2Br by far infrared laser magnetic resonance (FIR- LMR) spectroscopy.

The radicals were prepared either by mixing CH_3Br with the products of a microwave discharge in F_2/Ar or CF_4/Ar mixtures, or by reacting Na atoms in an Ar or He flow with CH_2Br_2. 84 different wavelengths between 230 and 1300μm were tried using the reaction of F atoms with CH_3Br as a source. Spectra of CH_2Br along with C, CH, CH_2, CH_2F, CCH, CF, and $CF^{\dagger}$, were detected at 37 of these wavelengths. In order to differentiate between CH_2Br spectra and the spectra of other species, the latter were either calculated using well known parameters or their dependence on the presence of Br was examined by using CH_4 or CH_3F as precursor instead of CH_3Br. Spectra at 12 wavelengths were attributed to CH_2Br.

The identification of CH_2Br as the carrier of the spectra is based on the following evidence: (1) Representative spectra at 672.1 and 447.3μm were reproduced with almost the same S:N ratio from both source reactions. (2) The spectra of CH_2 at 680μm were observed from $Na+CH_2Br_2$ and this confirms the presence of its precursor, CH_2Br. (3) Replacement of CH_3Br by CD_3Br gave different spectra or no spectra at all.

A complete spectroscopic analysis is not yet available due to the congestion of most of the spectra. Nevertheless, quite reliable values of (B+C) for both CH_2Br and CD_2Br can be deduced assuming CH_2Br is planar and therefore a near prolate rotor exhibiting only a-type transitions described by $\nu_0=(B+C)\ (N+1)$. A fit of all the laser frequencies at which CH_2Br spectra were observed to this formula yields 0.7443(51) and 0.6210(65)cm^{-1} for (B+C) for CH_2Br and CD_2Br respectively. A comparison of the bond lengths and angles in related radicals and saturated precursors suggests that a reasonable structure for CH_2Br might be r(C-H)=1.086Å, r(C-Br)=1.845Å and $\angle$HCH=124° which yields (B+C)=0.7446 and 0.6181cm^{-1} for CH_2Br and CD_2Br respectively.

Perturbations in the $B^3\Sigma^-$ state of the SO radical

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The $B^3\Sigma^- - X^3\Sigma^-$ transition of the SO radical has been reinvestigated in emission at high resolution using a Fourier transform spectrometer. The spectra of two isotopomers ($^{32}S^{16}O$ and $^{32}S^{18}O$) have been analysed in order to provide improved molecular constants for both states involved and to identify new perturbed levels. Approximate constants for the perturbing $C^3\Pi$ state will also be presented.

PRESSURE AND TEMPERATURE DEPENDENCE OF THE REACTION BETWEEN CH_3 AND OH RADICALS

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The kinetics of the reaction between CH_3 and OH radicals was studied at five temperatures between 283 and 373 K and in the pressure range of 85-1000 mbar SF_6. The experimental technique was pulse radiolysis combined with time resolved UV spectroscopy. Both CH_3 and OH radicals were monitored. The results from the measurements at room temperature, that were already published [1], show that the rate constant for the cross-reaction of CH_3 radicals with OH vary from $(5.8\pm0.3)\times10^{10}$ $M^{-1}s^{-1}$ at 85 mbar SF_6 to $(7.8\pm0.7)\times10^{10}$ $M^{-1}s^{-1}$ at 1000 mbar SF_6. The results of the present study clearly show that the pressure dependence of the rate constant is more pronounced at higher temperatures. Our experimental results will be analyzed following the concepts of Troe and co-workers [2-4]. In these analysis also literature data from shock-tube measurements at temperatures exceeding 1000 K will be taken into account.

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ELECTRONIC ENERGY TRANSFER BETWEEN SINGLE VIBRATIONAL LEVELS OF CN ($A^2\Pi_i$) AND ($X^2\Sigma^+$)

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Collisional energy transfer rate constants have been measured from a number of vibrational levels of the $A^2\Pi_i$ and $X^2\Sigma^+$ states against a variety of collision partners, including all of the noble gases, nitrogen and carbon dioxide. Radiative lifetimes have also been measured for individual vibrational levels of the $A^2\Pi_i$ state. CN was formed by 193 nm photolysis of C_2N_2 and excited by a Nd-YAG pumped dye laser. Transfer from the A to the X state is roughly an order of magnitude faster than transfer from the X to the A state. In all cases except one, the only observed process is transfer to the next lowest lying level of the other electronic state. Vibrational energy transfer does not compete against the electronic energy transfer. The single exception is that carbon dioxide quenches $A^2\Pi_i$ $v' = 4$ to both the $X^2\Sigma^+$ $v'' = 7$ and 8 levels. The former is a resonant process involving the v_3 mode of CO_2.

HIGH RESOLUTION XUV-LASER SPECTROSCOPY ON H_2

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High resolution measurements on two Lyman bands of molecular hydrogen have been performed near 97 nm. Rotational lines with a linewidth of 0.23 cm^{-1} were obtained from a sub-Doppler crossed beam configuration. The XUV-radiation needed for this purpose is produced in the following way. A dye-laser is pumped by a frequency doubled Nd:YAG-laser (532 nm) to produce light in the 580-590 nm region. This tunable radiation is frequency doubled after which the XUV-photons are produced by frequency tripling in a xenon-jet. The H_2 spectrum is recorded by 1 XUV + 1 UV photoionization and simultaneously an iodine[1]- and etalon spectrum are recorded in the visible (figure 1). The frequency of the XUV-light is then given by the energy of the fundamental wave multiplied by six. With the etalon spectrum we compensate for deviations from a linear wavelength-scan. By using computerized linearization and interpolation the H_2 transition frequencies could be determined to within 0.01 cm^{-1}. Because the measurements are very time-consuming we have measured only a few rotational transitions of the B-X(10,0)- and the B-X(11,0)-band. The obtained frequencies are compared with old[2] and recent less accurate measurements[3].

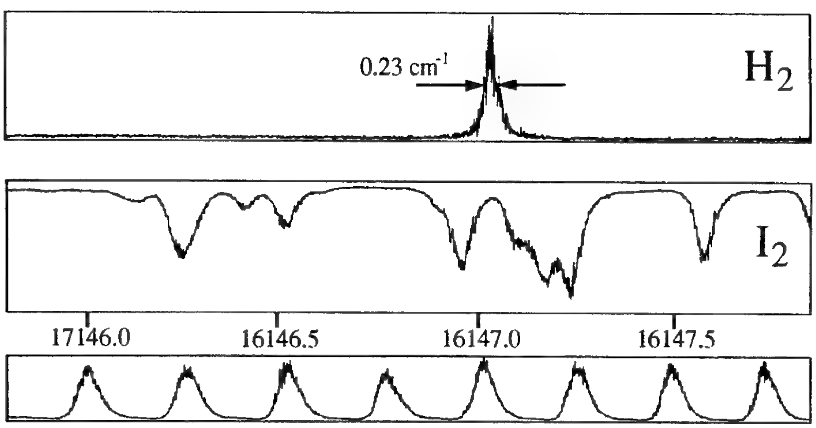

Figure 1: Simultaneously recorded spectra of the B-X(11,0) R(0)-line, I_2 and etalon.

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Microwave Spectra of the Open Shell $ArNO_2$ Complex

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Open shell complexes have attracted considerable attention recently. The interaction of a radical and a closed shell molecule allows the study of bonding, intermediate between chemical and physical. Also, the long range coupling of electronic spin and orbital angular momenta to intermolecular motion is important in the chemistry of free radicals. The high resolutiom offered by microwave spectroscopy allows these interactions to be probed in great detail. However, previously, only ArNO and ArOH have been studied by this technique.

We present here spectra of the $ArNO_2$ complex observed using Fourier transform microwave spectroscopy in the range 6 to 18 GHz. The unpaired electron is responsible for a large Zeeman splitting in the earth's magnetic field and this proved helpful in assigning the fine-structure.

Each rotational level has 5 or 6 fine/hyperfine structure states associated with it due to an electron spin angular momentum of 1/2 and the N atom nuclear spin of 1. Interactions of these momenta provide a rich source of information on the structure of the complex, including any effect the Ar has on the NO_2 electronic distribution. Analysis of the spectra is in progress.

Laser–Induced Fluorescence Spectra of Vibrationally Excited SiH_2: Vibrational Analyses of the $\tilde{X}$ and $\tilde{A}$ states

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Vibrationally excited SiH_2 ($\tilde{X}$) radicals were produced by the photolysis of jet–cooled phenylsilane at 193 nm and the laser–induced fluorescence (LIF) excitation spectra were recorded 1 μsec after the photolysis. On the basis of the LIF spectra, the vibrational analysis of the $\tilde{X}$ state including the Fermi resonances were carried out.[1,2] The resonaces occur between the (v_1, v_2+2, v_3) and the (v_1+1, v_2, v_3) states. The Fermi interaction energies W of these groups can be expressed as follows.

$$W_{v_1\ v_2+2\ v_3\ ,\ v_1+1\ v_2\ v_3} = C\sqrt{(v_1+1)(v_2+1)(v_2+2)}\ ,$$

where C is a constant. According to this equation, vibrational constants ω_1^0, ω_2^0, the anharmonic terms x_{11}, x_{12}, x_{22} and the Fermi interaction energy were determined and listed in Table I. In the course of this study, the vibronic bands terminated to the v_1 excited levels were observed for the first time.[2] The vibrational analysis using these transitions reveals the v_1 frequency to be 1990 cm^{-1}.

Table I. The vibrational constants and the Fermi interaction energy between the (020) and (100) levels of SiH_2 $\tilde{X}$ $^1A_1$.

constant	value / cm^{-1}
ω_1^0	1982.78 ± 0.51
x_{11}	2.97 ± 0.16
ω_2^0	1002.85 ± 0.20
x_{22}	−2.40 ± 0.18
x_{12}	−18.31 ± 0.60
$W_{020,100}$	11.96 ± 0.15

Reference

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EFFICIENCY OF INITIATION BY AZODIIZOBUTIRONITRILE AND DICYCLOHEXYLPEROXYDICARBONATE IN MICELLAR SOLUTIONS

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The reference publications are of little data on kinetic characteristics of decomposition of initiating agents in microheterogeneous systems. The inhibitors technique has been used to measure the free radicals formation rates at thermal decomposition of azodiizobutyronitrile (AIBN) (60°) in aqueous micellar solutions of cationic (cetyltrimetylammonium bromide, CTAB) and anionic (sodium dodecylsulfate, SDS) surfactants. The inhibitors (InH) used were of various nature: diphenyl-para-phenylenediamine (PhDA), 3,5,7,3',4'-pentahydroxyflavon (Q) and 4-(spiro-tetrahydrofuryl-2')-2-spirocyclohexyl-1,2,3,4-tetrahydroquinoline-1-oxyl (>NO·). The initiation efficiency 2e (see Table) was calculated with equation: $2e = f(d[InH]/dt)/k_d[AIBN]$, where f is stoichiometric coefficient of chain termination by inhibitor, k_d is the constant of decomposition rate for AIBN.

System	InH	f	2e
CTAB	PhDA	2	0,6
0,011 M	Q	2	0,7
	>NO·	1	0,5
SDS	PhDA	2	0,8
0,34 M	Q	2	0,7
	>NO·	1	0,5

The resulting values are apparently characteristics for maximum initiation efficiency when oil soluble initiator is used.

The thermal decomposition of dicyclohexylperoxydicarbonate (PC) has been studied in micellar solutions of various surfactants. In DDS solution the decomposition rate constant is practically coincident with that in n-decane: $\lg k_d = 15{,}44 - 29700/4{,}576T$. It has been established that PC reacts directly with CTAB, PhDA and >NO· under ambient conditions.

AB INITIO STUDY OF SOME LOW-LYING ELECTRONIC STATES OF THE $C_2H_2^+$ RADICAL ION

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Complete-Active-Space SCF (CASSCF) and Multi-Reference Configuration Interaction (MR-CI) calculations were performed employing large Gaussian basis sets of the general contraction type to determine the equilibrium structures and relative stabilities of the ground electronic state $\tilde{X}^2\Pi_u$ of the acetylene cation $C_2H_2^+$ and its low-lying excited electronic states, the $\tilde{A}^2\Sigma_g^+$ and $\tilde{B}^2\Sigma_u^+$ states, as well as their HCC-H dissociation behavior. While the $\tilde{X}$ and $\tilde{B}$ states have linear equilibrium structures, the first excited $\tilde{A}$ state was found to have a *trans*-bent equilibrium geometry with a bond angle of approximately 112^0. The C-H bond dissociation energy of the ion and parent neutral ground states were obtained in very good agreement with experimental findings, whereas the first ionization potentials of C_2H_2 and C_2H derived from the differences between the energies of the ion and the parent neutral were found to be systematically too small by about 0.2 eV. The present results were used to set a theoretical lower limit of 17.30 eV for the appearence energy of the C_2H^+ radical ion formation by dissociative photoionization of C_2H_2 and to discuss possible reaction pathways for this process. Additional calculations were performed to determine resonance states for the electron - ion recombination and possible dissociation channels for stabilizing the electron capture process. A qualitative picture for the low-energy dissociative recombination of $C_2H_2^+$ is thus obtained.

DISSOCIATIVE RECOMBINATION OF COOL MOLECULAR IONS IN THE ION STORAGE RING CRYRING

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Dissociative recombination is a complex process which occurs when a molecular ion captures a free electron, recombines and then subsequently decays by unimolecular decomposition into neutral fragments. The cross section for the process scales approximately as 1/E, where E is the collision energy. Hence, in order to obtain meaningful results, the process must be studied at collision energies much smaller than one eV. The merged-beam technique offers means to obtain low energy collisions between electrons and ions, and a recent, and very powerful, development is to apply ion storage ring technology to this end. The molecular ions are stored at high energy (tens of MeV), and are circulated a million times per second through the electron target. This greatly enhances the effective current. Moreover, the electron beam can also be used to phase-space compress the molecular ions (electron cooling), which means that the energy spread in the ion beam is reduced significantly. The most important advantage, however, is that storage of the molecules for tens of seconds allows them to relax down to their vibrational ground state by emission of infrared radiation (radiative cooling).

The storage ring CRYRING in Stockholm has recently been used for dissociative recombination experiments with H_3^+ and HeH^+.[1]

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parity resolved rotational excitation in inelastic NO - Ar scattering

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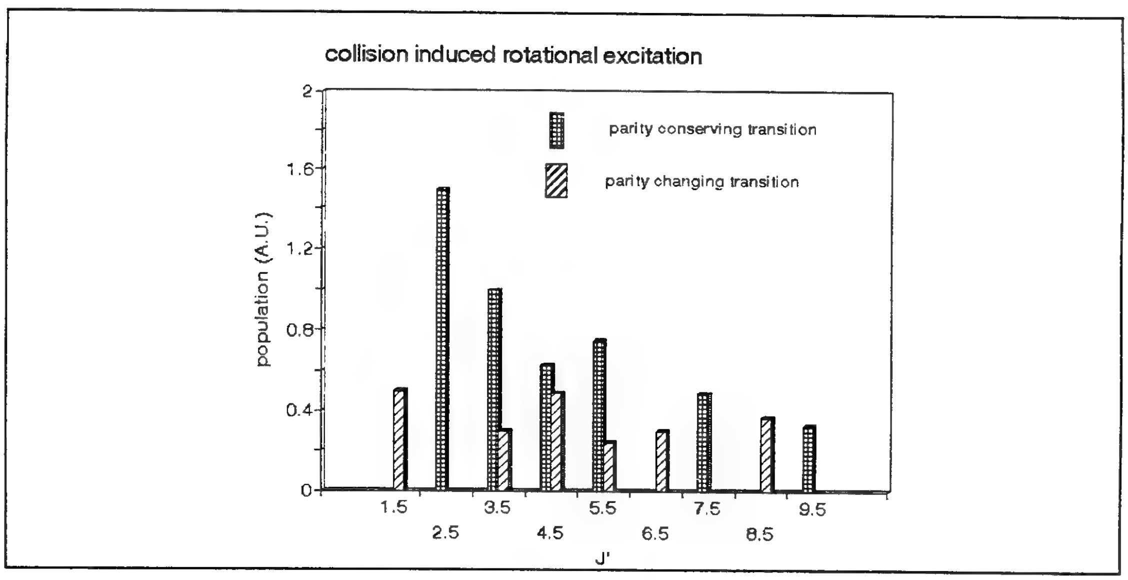
Of a pulsed beam of NO molecules in the electronic ground state the upper Lambda component of the J = 0.5 rotational state is focused with an electric hexapole lens on the scattering centre. At the scattering centre the state selected NO molecules are impinging onto a pulsed Ar beam with a collision energy of $E_{tr}\approx 50$ meV. To allow studies of orientational dependent effects an assembly yielding a homogenous electric field at the scattering centre has been constructed. The resulting collision induced rotational state distribution is probed by Laser Induced Fluoresence via the electronic A state.

In addition to the expected propensity of parity conservation our first results (see figure) exhibit a fair amount of parity changing collisions. From this latter effect we infer the presence of an appreciable contribution of odd-Legendre polynomial terms in the Ar-NO interaction potential. As predicted by theory parity changing collisions occur more likely for odd ΔJ transitions as can be observed underneath.



Population distribution of inelastic scattered NO molecules in the electronic ground state $^2\Pi_{1/2}$. Both the tendency for parity conserving transitions over parity changing as well as an oscillating behavior with odd/even ΔJ is observed.

Velocity modulation spectroscopy on electronic transitions of some diatomic ions

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The Velocity Modulation technique[1] and a Coherent 699-29 Autoscan system has been used to reveal the usually weak absorption of the diatomic ions N_2^+, C_2^-, C_2^+, and Br_2^+ in a gas discharge. Absorption close to $1:10^6$ could be detected. The spectra of the corresponding neutral molecules were suppressed at least 500 times.

The lineshape broadening, resulting in less precise determination of line center positions and frequent overlapping of lines, were reduced by the fitting and decomposition into separate line profiles. For that purpose a PC program where different syntetic profiles can be fitted to observed lines was used. Also, distorsions caused by the time constant during the recording of spectra can be accounted for. A precision and resolution of about 0.005 cm^{-1} were obtained.

Rotational analyses and deperturbation of different band systems have been performed for the following molecular ions:

Molecule	Transition	Band
N_2^+	$A^2\Pi_u - X^2\Sigma^+_g$	(8,3) (9,4) (11,5)
	$B^2\Sigma^+_u$-$X^2\Sigma^+_g$	(1,5)
C_2^-	$B^2\Sigma^+_u$-$X^2\Sigma^+_g$	(0,0)
C_2^+	$B^4\Sigma^-_u$-$X^4\Sigma^-_u$	(0,1)
Br_2^+	$A^2\Pi_u$-$X^2\Pi_g$	27 bands were included in the analysis

Reference

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THE PREDICTION OF BOND DISSOCIATION ENERGIES FOR COMMON ORGANIC COMPOUNDS

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To predict bond dissociation energies (BDEs) is a major goal for physical chemists. In 1988 and 1990 Griller et al stated that: no satisfactory approach has yet emerged [J. Mol. Struc. (Theochem.), 1988, 163, 125, and in "Adv. Free Radical Chemistry" Vol. 1, 1990, p. 159]. The present authors have shown that this important problem can be resolved, step by step. The key component of the work reported here is the use of "the covalent potential", V_x, associated with a new scale of electronegativity[1]. The appropriate simple equation is

$$BDE(C\text{-}X)_{est} = BDE(X\text{-}CH_3)_{obs} - m \frac{6.33 + 0.36m - V_x}{0.67 + 0.21m} + \Delta V_{nb} \qquad (2)$$

Here V_x is the covalent potential of X; m is the degree of methyl substitution and represents primary, secondary and tertiary alkyl groups when m = 1, 2 and 3, respectively; ΔV_{nb} is the steric compression relief, that is, the net change of the steric interaction energies between the non-bonding atoms from the given molecule to the free radicals resulting from the bond cleavage. The average deviation using eq. (2) for 65 observed X-C BDEs in Griller's work is less than 0.6 kcal/mol.

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Frequency-Modulation Enhanced Magnetic Rotation Spectroscopy: A Sensitive and Selective Detection Scheme for Paramagnetic Molecules

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The technique of frequency-modulation enhanced magnetic rotation spectroscopy (FM-MRS) is described. A comparison between FM-MRS, frequency modulation (FM), and magnetic rotation spectroscopy clearly demonstrates that this *double null* absorption-based technique is at least an order of magnitude more sensitive than either FM or magnetic rotation spectroscopy separately. The theoretical basis for this sensitivity enhancement can be attributed to a $1/\theta$ (where θ is the small uncrossing angle between two nearly crossed polarizers) improvement in the signal-to-noise and sensitivity of the combined FM-MR technique relative to the standard FM spectroscopy. In practical terms, this enhancement can improve the experimentally achievable sensitivity of standard FM spectroscopy by a factor of 10-100, and to a level that approaches the theoretical quantum noise limit of this technique. In addition, because FM-MRS is based on the Zeeman effect, Zeeman information is encoded into the FM-MR line profiles in the form of relative phase labels and lineshapes. The relative phases and lineshapes of a rotational line can be used to group features by rotational branch and to differentiate between magnetically active ($\Lambda \neq 0, \Sigma \neq 0$) and inactive ($\Lambda = 0, \Sigma = 0$) features. The theory of FM-MRS, including a discussion of lineshapes and a sensitivity analysis will be presented. In addition, experimental FM-MR results for several bands of PdH, PdD, NiH, and CuH will also be presented. In the case of PdH, we have observed and assigned an Ω=0.5 – XΩ=0.5 band at 4371 Å. Prior to this work, although several bands of PdD had been reported previously, no electronic transitions of PdH had been assigned. All of the PdH, PdD, and NiH bands we have studied in the 4200-4600 Å wavelength region are strongly predissociated, and in the case of PdH and PdD, strongly and multiply perturbed as well.

Faraday Laser Magnetic Resonance Spectroscopy of vibrationally excited C_2H

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The vibronic spectrum of the ethynyl radical C_2H is complicated because of the coupling between the electronic ground state $\tilde{X}^2\Sigma^+$ and the $\tilde{A}^2\Pi$ state. A Faraday-L.M.R.-spectrometer with a CO-overtone laser has been used to study the gas-phase spectrum of C_2H in the region around 3300 cm^{-1}. The C_2H molecules were produced in a normal dc-discharge in a mixture of helium and acetylene. Transitions of a new band with origin at 3321 cm^{-1} connecting known levels could be observed and analyzed. The lower state was found to be the first excited bending-level (0,1,0) of the electronic ground state [1,2,3]. The upper level could be identified as a vibronic $^2\Pi$ level with T_{vib} = 3693 cm^{-1} [2,3] which corresponds to a mixture of a vibrationally excited level of the electronic ground state and the (0,0,0) level of the $\tilde{A}^2\Pi$ state. It was possible to determine the orbital g-factor g_L of the upper level, which is a measure of the mixing between $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states. This can be compared with theoretical results [4].

References

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ROTATIONAL, FINE AND HYPERFINE ANALYSIS OF THE $D^3\Pi$-$X^3\Delta$(0,0)BAND OF VANADIUM MONONITRIDE

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The VN molecule has been produced in a molecular beam apparatus using a laser vaporization source and its $D^3\Pi$-$X^3\Delta$(0,0) band has been studied by laser-induced fluorescence at low (~ 0.1 cm^{-1}) and sub-Doppler resolution (~ 0.004 cm^{-1}). Rotational, fine and hyperfine structures in six of the nine sub-bands possible for a $^3\Pi \leftarrow {}^3\Delta$ transition have been recorded. Both states exhibit a rapid transition from case (a) → case (b) coupling cases, manifested by reversals in the Landé patterns of the hyperfine structure. The data have been reduced to a set of 35 molecular constants using a modified case (a_β) effective Hamiltonian in which two additional magnetic hyperfine parameters are required for each state. The distortions in the hyperfine structure are almost entirely due to second-order spin-orbit interaction between states arising from the same configuration. Analysis of the derived parameters indicates that the $X^3\Delta$ state is well represented by the single electron configuration ...$8\sigma^2\ 3\pi^4\ 9\sigma^1\ 1\delta^1$, in which the 9σ molecular orbital (MO) is a V 4s-4p hybrid (88% V 4s) and the 1δ MO is a pure V 3d orbital; the dominant configuration for the $D^3\Pi$ state is ...$8\sigma^2\ 3\pi^4\ 1\delta^1\ 4\pi^1$, in which the 4π MO is an antibonding orbital composed of at most 82% V $3d\pi$. The isoconfigurational $a^1\Delta$ and $e^1\Pi$ states are calculated to lie 3390 and 2200 cm^{-1} above their respective high spin companions.

NEW SPECTRA OF SiH^+ AND SiD^+

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Extensive series of new emission bands of SiH^+ and SiD^+ spectrum have been observed in the region 170 nm - 200 nm from a high frequency discharge through a mixture of a trace of $SiCl_4$ in helium and hydrogen. This spectrum has been recorded at high resolution by a 6.6 m vacuum spectrograph. Rotational and vibrational analyses are carried out and molecular constants of the electronic states are determined. The rotational structure follows a simple $^1\Sigma$ - $^1\Sigma$ transition. Ten bands of SiH^+ and fifteen bands of SiD^+ are explained as transitions between two new excited electronic levels and the lowest $^3\Pi_0$ state predicted from theoretical calculations.[1] The carrier of the spectrum is confirmed by the observed isotopic effect.

References

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Double-Resonance spectroscopy, a powerful tool for the study of highly excited electronic states of molecules

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A spectrometer has been built to study highly excited electronic states (E>8 eV) of molecules by double-resonance spectroscopy. Molecules in a molecular beam, *e.g.* radicals produced by an electric discharge[1] or by laser evaporation[2], are resonantly 2-photon excited by a pulsed dye laser to a high-lying electronic state. In a second step the molecules are 1-photon excited from this level to a still higher lying electronically excited state. Transitions to this state can be detected either by observing the fluorescence from this state to lower lying states or by monitoring the fluorescence loss of the intermediate state. Employing a single-frequency cw ring dye laser or a pulsed dye amplifier system in the second step the highly excited state can be studied at high resolution (10-200 MHz).

This technique has been tested on the CO molecule. After populating in the first step the B $^1\Sigma^+$ state, in the second step Rydberg states at 103 000 cm^{-1} are probed. In this way not only accurate molecular constants could be obtained for the Rydberg states but also predissociation rates for these states could be determined from the observed linewidths.

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[2]M. Ebben, G. Meijer and J.J. ter Meulen, Applied Physics B **50**, 35 (1990)

INDEX OF CONTRIBUTIONS

Participant	Abstract	Participant	Abstract
M. Ashfold	I-1	G. Hancock	I-15
S. Ashworth	A-2	G.M. Hansford	B-3
F. Askar	A-3	B. Hanoune	B-8
N. Balucani	A-1	M. Havenith	B-9, C-20
G. Berden		J. Heinze	A-10
K. Bergmann	B-13	P. Hinnen	C-10
E. Bieske	I-17	Y.-C. Hsu	B-2
B. Bohn	B-1	J.M. Hutson	I-11
M. Boogaarts	B-16	H. Ishikawa	C-12
H.B. Bredohl	A-8	M. Jacox	B-5
J. Breton		M.H.M. Janssen	B-15
J.M. Brown	A-2, C-2, C-3	J. Kappert	B-7
C.H. Bryant	A-4	Z.S. Kartasheva	C-13
A. Carrington		O.T. Kasaikina	A-19, B-11, C-13
R. Colin	C-7	V. Khmelenko	C-1
A. Cooksy	I-6	K. Kohse-Hoinghaus	A-10
L. Cotarca	B-19	W.P. Kraemer	C-14
R.F. Curl	A-5	G.-J. Kroes	B-12
P.J. Dagdigian	I-8, C-5	A. Kuhn	B-13
P.B. Davies	A-4, B-3, C-6	A. Largo	A-12
C.A. de Lange	I-18	M. Larsson	C-15
C. Demuynck	I-9	J. van Leuken	C-16
E.F. van Dishoeck	I-5, B-12	B. Lindgren	A-6, B-4, C-17
C. Domingo	A-22	C. Linton	A-13
M. Drabbels	C-23	H. Linnartz	B-9
A. Dymanus		Y. Liu	C-6
A.M. Ellis		Y.-R. Luo	A-14, C-18
Y. Endo	I-10	A. Marijnissen	
K.M. Evenson	A-2, C-2, C-3	E. Martinez	B-14
K. Fagerstrom	A-18, C-8	M. McCarthy	A-15, C-19
A. Farkhsi	A-8	D. McLay	
E.H. Fink	I-14	W.L. Meerts	C-23
R. Friedl	B-6	A.J. Merer	I-20, C-21
A. Geers	B-7	J.J. ter Meulen	I-7, C-23
G. Guelachvili	I-13, B-8	G. Meijer	B-16
S.N. Ghosh		R.J. Miller	A-16
W. Hack	A-9	T.A. Miller	I-12
P.A. Hackett	I-19, A-20, C-21	I.I. Morozov	A-7
J.B. Halpern	C-9	A. Nada	B-17

Participant		Abstract
T. Nakanaga		B-18
D.M. Neumark		I-2
P. Pagsberg		A-18
D.H. Parker		B-16
C. Pfelzer		C-20
H.E. Radford		B-20
E. Ratajczak		A-18, C-8
L. Santos		B-14
T.J. Sears		A-4, B-20
B. Simard		A-13, A-20, C-21
Ch. Stöck		B-7
S. Stolte		B-15, C-10, C-16
F. Stuhl		B-1, C-4
L. Sukhanov		B-12
V. Szalay		A-21
V.L. Tal'rose	K. Tanaka	B-22
I. Tanarro		A-22
M. Tanimoto		A-11
F. Temps		I-3, B-7
E. Tiemann		I-4
W. Ubachs		C-10
R.D. Verma		C-22
C. Whitham		C-11
J. Wolfrum		I-16
W. van der Zande		B-10

Program of the 22nd International Symposium on Free Radicals. September 6-10, 1993, Doorwerth, The Netherlands.

	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday
8.55 9.00 9.45		OPENING M.N.R. Ashfold D.M. Neumark	E.F. van Dishoeck W. Cooksy	C. Demuynck Y. Endo	G. Guelachvili E.H. Fink	A. Bieske C.A. de Lange
10.30		Coffee	Coffee	Coffee	Coffee	Coffee
11.00 11.45 12.30		F. Temps E. Tiemann	J.J. ter Meulen P.J. Dagdigian	J.M. Hutson T.A. Miller	G. Hancock J. Wolfrum	P.A. Hackett A.J. Merer CLOSING
12.30		Lunch	Lunch	Lunch	Lunch	Lunch
14.00 15.00	REGISTRATION DESK OPEN (Untill midnight)	Poster Session A Introduction Poster Presentation A (tea)	EXCURSION 't Loo	FREE AFTERNOON	EXCURSION Kröller-Müller Museum	
18.00		Dinner	Dinner	Dinner		
19.30 20.30	WELCOME RECEPTION	E. Boersma	Poster Session B Introduction Poster Presentation B (coffee)	Poster Session C Introduction Poster Presentation C (coffee)	CONFERENCE DINNER	